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Catalytic Hydrodechlorination of Polychlorinated Pesticides and Related Substances: An Executive Summary

Eben Research Systems, Silver Springs, Md

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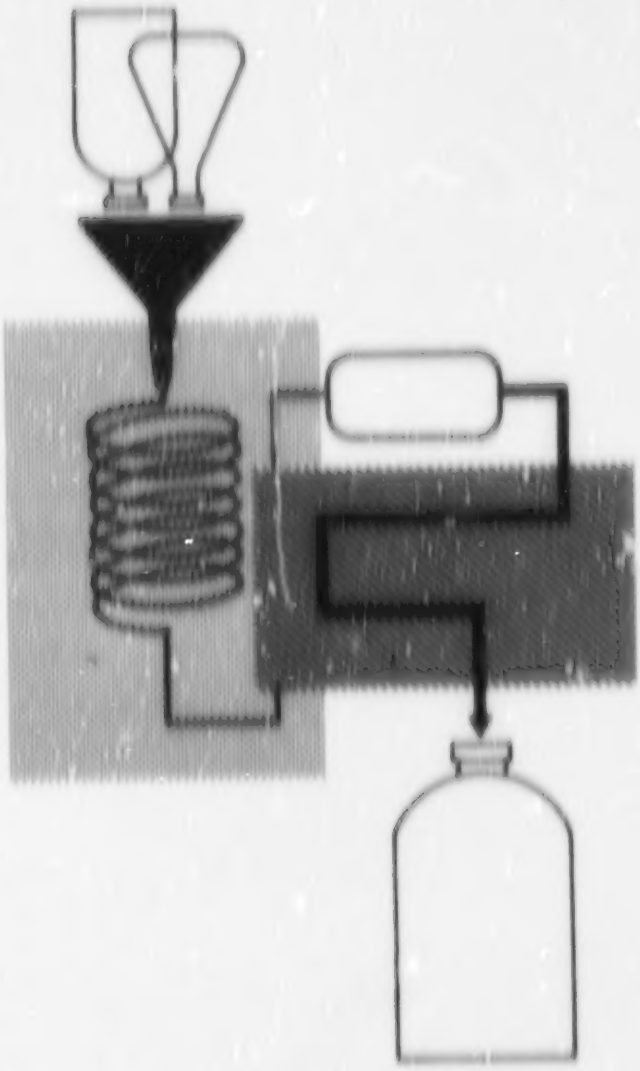

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16. ABSTRACT

A study was undertaken of the catalytic conversion of chlorinated pesticides and other undesirable chlorinated compounds to acceptable compounds. This study shows that chlorine can be catalytically removed and replaced by hydrogen to produce relatively non-toxic hydrocarbons.

The batch process involves use of a supported nickel catalyst, ethanol as solvent, and sodium hydroxide as an acid-acceptor of the hydrogen chloride by-product.

A reactivity sequence is established based on carbon-chlorine bonding wherein olefinic chlorine is the least reactive. Reaction models are determined for Aroclor 1248 and DDE.

Removal of ortho-substituted chlorine is the limiting reaction in hydrodechlorination of Aroclor. Aldrin and dieldrin are the most difficult compounds to hydrodechlorinate because of steric hindrance. Removal of aromatic chlorine is the limiting reaction in the hydrodechlorination of DDT and DDE.

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CATALYTIC HYDRODECHLORINATION OF POLYCHLORINATED PESTICIDES AND RELATED SUBSTANCES

An Executive Summary

by

Ebon Research Systems
Silver Spring, Maryland 20901

Contract No. 68-03-2460

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ABSTRACT

A study was undertaken of the catalytic conversion of chlorinated pesticides and other environmentally undesirable chlorinated materials to acceptable compounds. The results of this study show that chlorine can be catalytically removed and replaced by hydrogen to produce relatively non-toxic hydrocarbons.

The experimental foundation for a hydrodechlorination process is established. This batch process involves use of a supported nickel catalyst, ethanol as a solvent and sodium hydroxide as an acid acceptor of the hydrogen chloride by-product. Temperatures less than 150°C and hydrogen pressures on the order of 50 atmospheres are required.

A reactivity sequence is established based on carbon-chlorine bonding wherein olefinic chlorine is the least reactive. Reaction models are proposed and the relative rates of steps in the reaction sequence are determined for Aroclor 1260 and DDE.

Removal of ortho-substituted chlorine is the limiting reaction in hydrodechlorination of Aroclor. Aldrin and dieldrin are the most difficult compounds to hydrodechlorinate because of steric hindrance. Removal of aromatic chlorine is the limiting reaction in the hydrodechlorination of DDT and DDE.

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We are indebted to the authors of CATALYTIC CONVERSION OF HAZARDOUS AND TOXIC CHEMICALS: CATALYTIC HYDROGENOLYSIS OF POLYCHLORINATED PESTICIDES AND RELATED COMPOUNDS, Rene D. LaPierre, Ehud Biron, David Wu, Laszlo Guczi, Wilmer L. Kranich and Alvin H. Weiss.

SECTION 1

INTRODUCTION

Many of the widely used insecticides and other organic chemicals that have been found to persist in the abiotic and biotic environments are chlorinated compounds. Stocks of these compounds, whose toxicity has warranted their restriction at the market, must be destroyed or converted to harmless biodegradable or potentially useful chemicals. Removal of some or all of the chlorine atoms generally effects this transformation.

Catalytic replacement of chlorine with hydrogen was the widely applicable process selected as the model system for this investigation. This process is adaptable to a trailer-mounted unit, an objective of some EPA officials. The compounds chosen for study were: (a) Aroclor 1248 (representative of polychlorinated biphenyls, PCB's); (b) 2,2- bis (p-chlorophenyl)-1,1,1-trichloroethane (DDT); 2,2-bis(p-chlorophenyl)-1,1-dichloroethylene (DDE);DDD, 2,2-bis(p-chlorophenyl)-1,1,-dichloroethane; (c) Dieldrin and aldrin; and (d) toxaphene. Extensive experimental data are reported for the first two classes, whereas limited data have been obtained for the latter two classes.

LITERATURE

Recent studies of hydrodechlorination according to the general reaction:

$$(1)\quad R\text{-}Cl + H_2 \longrightarrow R\text{-}H + HCl$$ (where R = alkyl, aryl, vinylic or allylic group)

have established that the ease of reaction is strongly dependent on the structure of the carbon associated with the chlorine. The above reaction is usually carried out in the presence of an acid acceptor such as NaOH. Carbon configurations encountered in the study were generally: mono and polychlorinated aliphatic, mono and dichlorinated vinylic and allylic, and aromatic. It has been reported that electron polarization followed by rupture of the C-Cl bond is the mechanism of dechlorination of mono- and dichlorinated butene (1-7).

Transition metals (Pt, Pd, Rh, Ni) are known to be effective catalysts, and the activity sequence Pd > Pt > Rh has been established for removal of chlorine from chlorinated benzene (8-12). Product inhibition of catalyst has been proposed, as catalyst activity in batch systems decreases with conversion (11-15). Presence of an acid acceptor has been shown to lessen damage to the catalyst (9). Reaction rates are affected by the solvent chosen for liquid phase reactions (12) and are related to catalyst activity.

the reactivity sequence:

$$-CH_2Cl < -CHCl- < \begin{matrix} Cl & Cl \\ | & | \\ -C & -C- \\ | & | \\ H & H \end{matrix} < \begin{matrix} Cl \\ | \\ -C \\ || \\ -C \end{matrix} - Cl$$

has been established for simple aliphatics. For simple compounds containing double bonds, the reactivity increases in the sequence; aliphatic chlorine, vinyl chlorine, olefinic chlorine (17-20).

For more complex molecules, it has been reported that PCB can be quantitatively hydrodechlorinated at 180°C, and that 1,1-dichloro, (2-bis-p-chlorophenyl) ethane is easier to hydrodechlorinate than trichloro, (2-bis-p-chlorophenyl) ethane (21).

This report addresses the question of whether or not chlorine atoms bonded to different groups in a single molecule retain the relative reactivity as determined from studies of simple molecules. It is also concerned with the relative hydrodechlorination activity of polychlorinated compounds.

SECTION 6

CONCLUSIONS AND RECOMMENDATIONS

This study established the hydrodechlorination stoichiometry of several pesticides and related substances. Results of preliminary process variable (temperature and H_2 pressure) studies were also obtained. It was found that a pulsed microreactor interfaced with a gas chromatography/mass spectrometry (GC/MS) facility is a powerful tool in determining catalyst activity and reaction selectivity, and that a continuous gas phase reactor is useful for evaluating catalyst stability. Liquid phase stirred reactors were used for obtaining kinetic data and establishing reaction paths. The liquid phase reactors would form the basis for the most feasible processing system.

The major conclusions drawn from the data obtained are as follows:

1) Inexpensive supported Ni catalysts, such as the 61% Ni on kieselguhr used in these studies, are adequate for the hydrodechlorination of pesticides and related substances. Reactions catalyzed with 10% Pd on charcoal exhibited similar stoichiometry to those observed with nickel. The apparent activation energies observed during liquid phase DDE hydrodechlorination were virtually identical on both catalysts. Liquid phase Ni catalyzed reactions must of course be carried out in the presence of an acid acceptor such as NaOH to avoid dissolution of the Ni metal. The Ni catalyst was observed to deactivate during aromatic hydrodechlorination at temperatures of 130°C and above, which places an upper limit on reaction temperature. When needed, higher catalyst loading may be used to increase specific rates in a constant volume reactor.

2) Polar solvents such as ethanol are recommended over hydrocarbon solvents such as xylene. Comparative experiments on DDT hydrodechlorination show that higher reaction rates and less complex product distributions are obtained when a polar solvent is used. Gas phase DDE kinetic studies also show that xylene competes for the catalyst surface and therefore acts as an inhibitor. In addition, polar solvents allow for the use of soluble acid acceptors such as NaOH, which increase observed reaction rates in the liquid phase.

3) Ni catalyzed Aroclor (PCB) hydrodechlorination is a consecutive process characterized by the number of chlorine atoms per molecule and the degree of ortho versus (meta plus para) chlorine substitution. The relative rate constants obtained by reaction path analysis indicate that product inhibition effects are expected in PCB hydrodechlorination. The relative hydrodechlorination rate of ortho versus (meta plus para) PCB isomers was determined to be 0.52. Removal of ortho substituted chlorine is the limiting step in complete hydrodechlorination of PCB.

4) DDT reacts rapidly with hydroxyl ions to produce DDE. DDE hydrodechlorination itself is characterized by concerted removal of both olefinic chlorines followed by rapid saturation of the dechlorinated olefin. Removal of aromatic chlorine from DDE is a stepwise process, and is the rate limiting step in producing the hydrocarbon product 1,1-diphenyl ethane. DDE hydrodechlorination is characterized by concerted removal of both aliphatic chlorines and stepwise removal of aromatic chlorine. Aliphatic hydrodechlorination is the rate limiting step for DDE. Olefinic hydrodechlorination is more pressure dependent than aromatic hydrodechlorination, and may be used to effect changes in intermediate selectivities. Liquid phase reactions, both Pd and Ni catalyzed, are characterized by concerted steps where both olefinic and aromatic chlorines are removed in one trip to the catalyst surface.

5) Aliphatic chlorines, while least reactive, may also be catalytically removed. Studies on toxaphene hydrodechlorination show that most of the chlorine is easily removed. The decreased reactivity of the remaining chlorine is believed to be due to steric effects.

6) Bridged non-planar compounds are the most difficult to react due to steric effects. Studies on aldrin and dieldrin hydrodechlorination show these compounds are the least reactive, even though they contain highly reactive olefinic chlorine. It appears that the non-chlorinated part of the aldrin structure is preferentially adsorbed, inhibiting the access of the chlorinated part of the molecule to the catalyst surface.

7) The liquid phase hydrodechlorination of pesticides and related substances is the favored process alternative for a large scale unit. The commercial utility of the partially and totally dechlorinated products has not been established, neither has a meaningful assessment of toxicity yet been made.

SECTION 3

MATERIALS AND METHODS

Design of an appropriate catalytic hydrodechlorination process involves selection from a wide variety of reactor configurations, reactant compositions, catalyst forms, and operating conditions. In this study the five reactors described below were used to investigate the possible modes of operation.

PULSED MICROREACTOR

The pulsed microreactor used (Figure 1) was the tubular glass liner of the injection port of a Perkin Elmer 900 gas chromatograph. The gas chromatograph could be connected to a mass spectrometer for product identification. Carrier gas transported the injected reactants through the reactor, which was placed in an aluminum heating block capable of varying temperature from ambient to 400°C. Catalyst beds, typically 2 to 10 mm long containing 2 to 10 mg, were pre-reduced with carrier gas (H_2) at 250°C. The organochlorine reactant (0.5 to 2µl) was then injected, and the reaction products monitored chromatographically. The residence time, calculated on the basis of carrier gas flow rate, was of the order of 10 seconds. The pulsed microreactor was employed as a screening device, allowing approximate determination of operating conditions.

CONTINUOUS VAPOR PHASE REACTOR

In the continuous flow process (Figure 2), the chlorinated organic was vaporized into a stream of hot carrier gas and was passed through a heated tubular (6mmID) glass reactor, where the gas reaction proceeded. The product collection device had a cold trap. Catalyst beds typically 1 to 5mm long containing 20-30 mg catalyst were located at the isothermal center of the tubular electric furnace. The solvent used in the reactor system was p-xylene. The total gas flow rate was measured with a bubble flow meter. The continuous reactor was well suited for catalyst deactivation studies.

LIQUID PHASE REACTORS

Batch processes studied employed supported metal catalysts slurried in a well stirred reaction vessel. This configuration allowed use of high pressure coupled with high temperature. Three reactors of this type were used:

(1) Low Pressure Glass Reactor

This reactor (Figure 3), designed to measure H_2 uptake and product

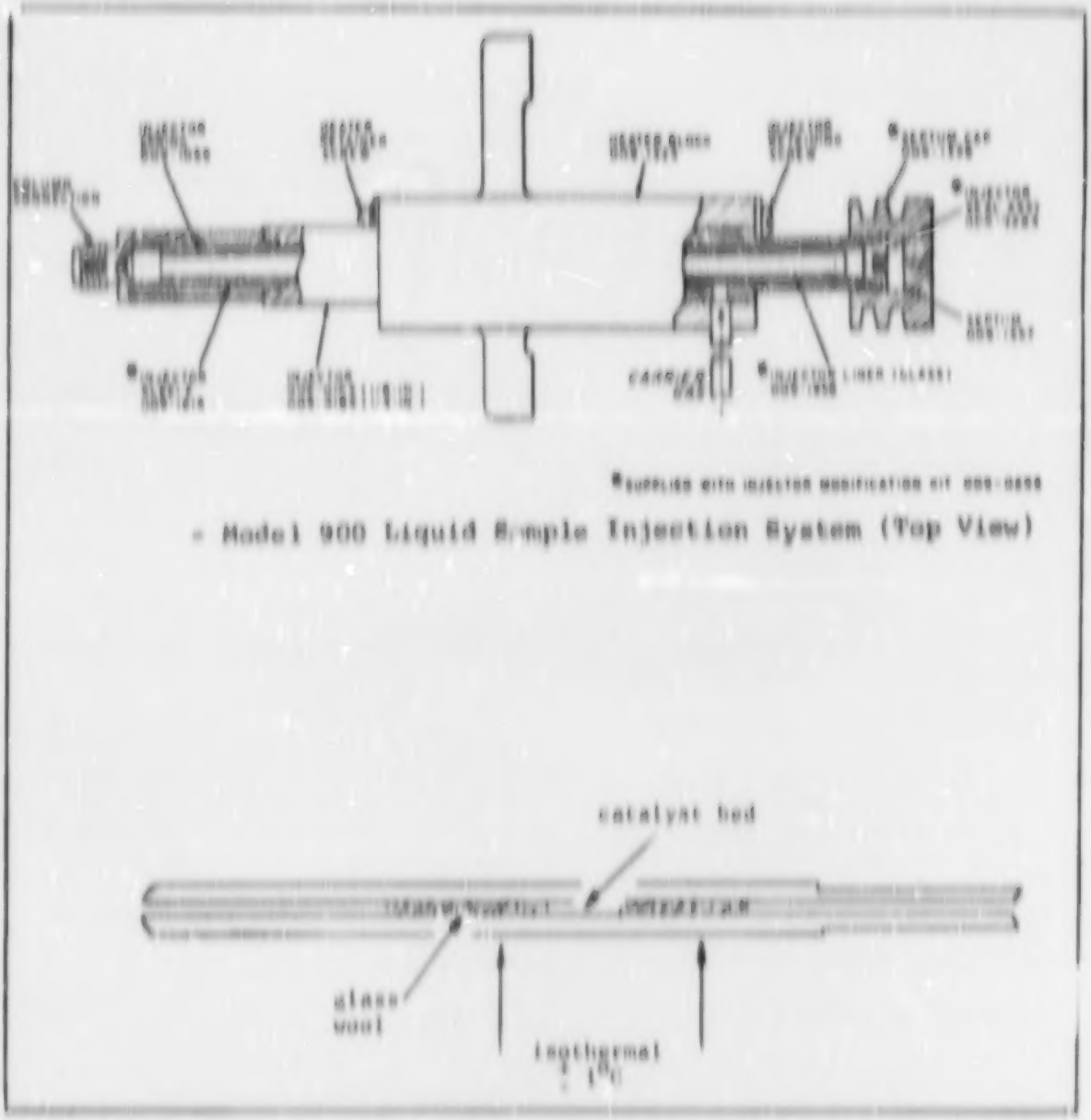


Figure 1. Pulsed microreactor

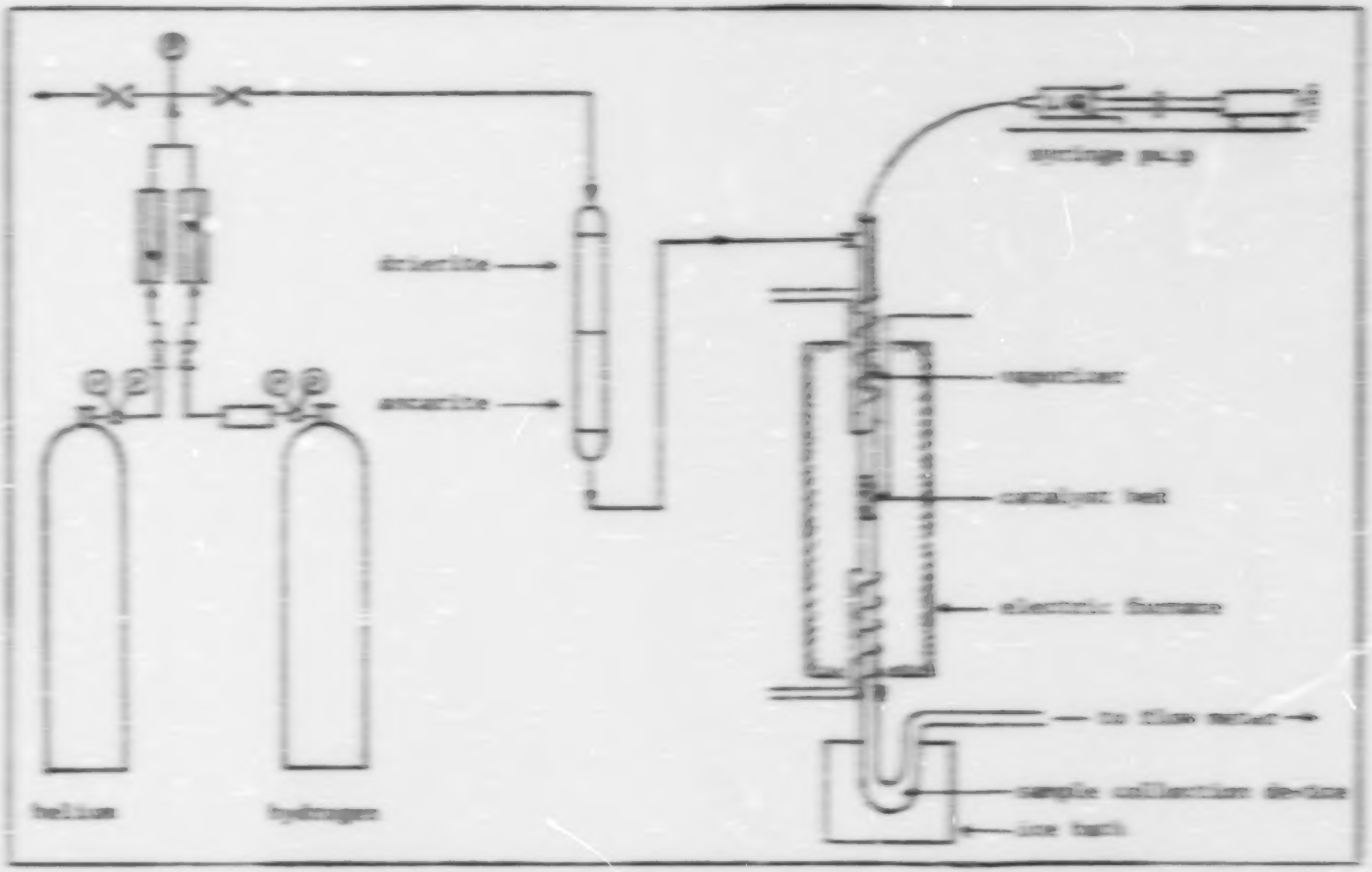


Figure 2.

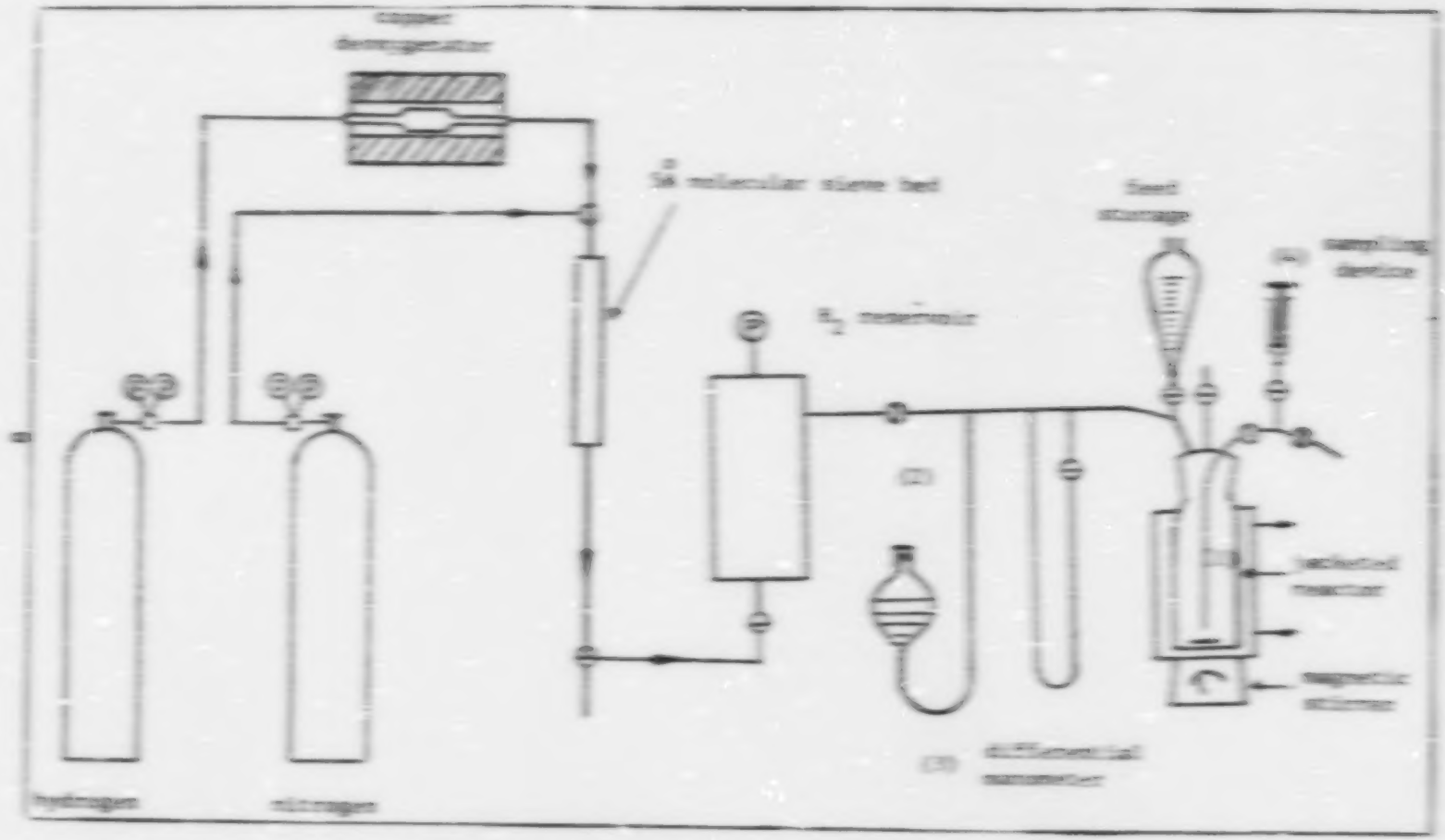


Figure 1. The pressure glass reactor

distribution simultaneously, was surrounded by a water jacket which was connected to a thermostat. The system included a mercury-filled burette for H_2 uptake measurement and a sampling port from which a small amount of product could be withdrawn for chromatographic analysis.

(2) High Pressure Stirred Reactors

(a) Teflon-Lined Autoclave

A 750cc teflon-lined autoclave (Figure 4) was used for liquid phase studies at elevated hydrogen pressures and temperatures up to 250°C. The autoclave was equipped with a stirrer, thermocouple, and high pressure sampling device. In the operating procedure, solvent, catalyst and acid acceptor were heated under a high pressure H_2 atmosphere to reaction conditions before H_2 was added by difference at time zero.

(b) Rocking Autoclave

Preliminary high pressure liquid phase experiments were conducted in a 100 cc glass-lined rocking autoclave (Figure 5), which could be operated at pressures up to 15,000 psi. The reactor shell was secured horizontally in a heating jacket and the entire unit was rocked to obtain mixing. This system was operated at 750 psi with time zero being the time at which H_2 was charged to the reactor.

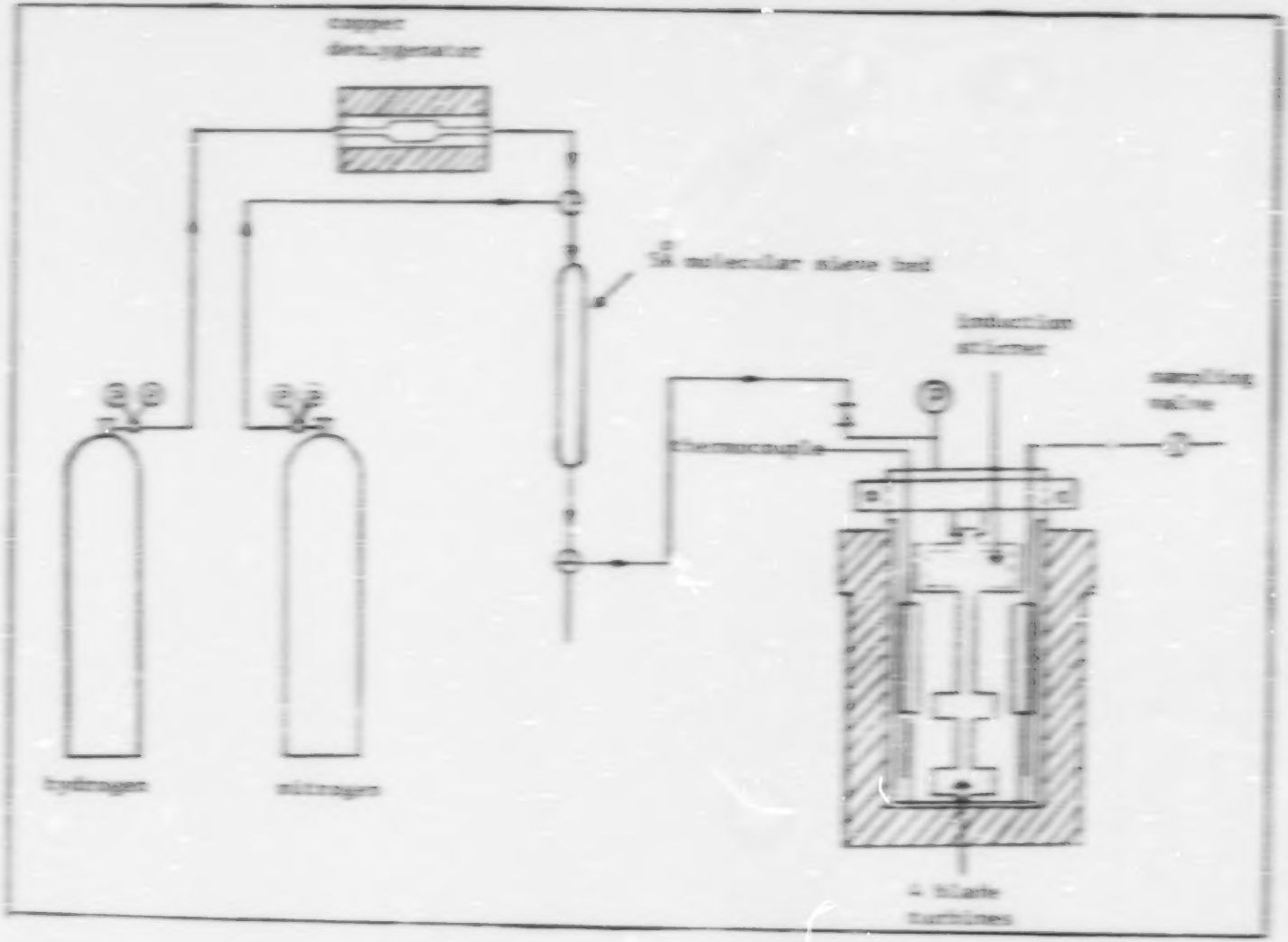


Figure 4. High pressure reflux-ing autoclave

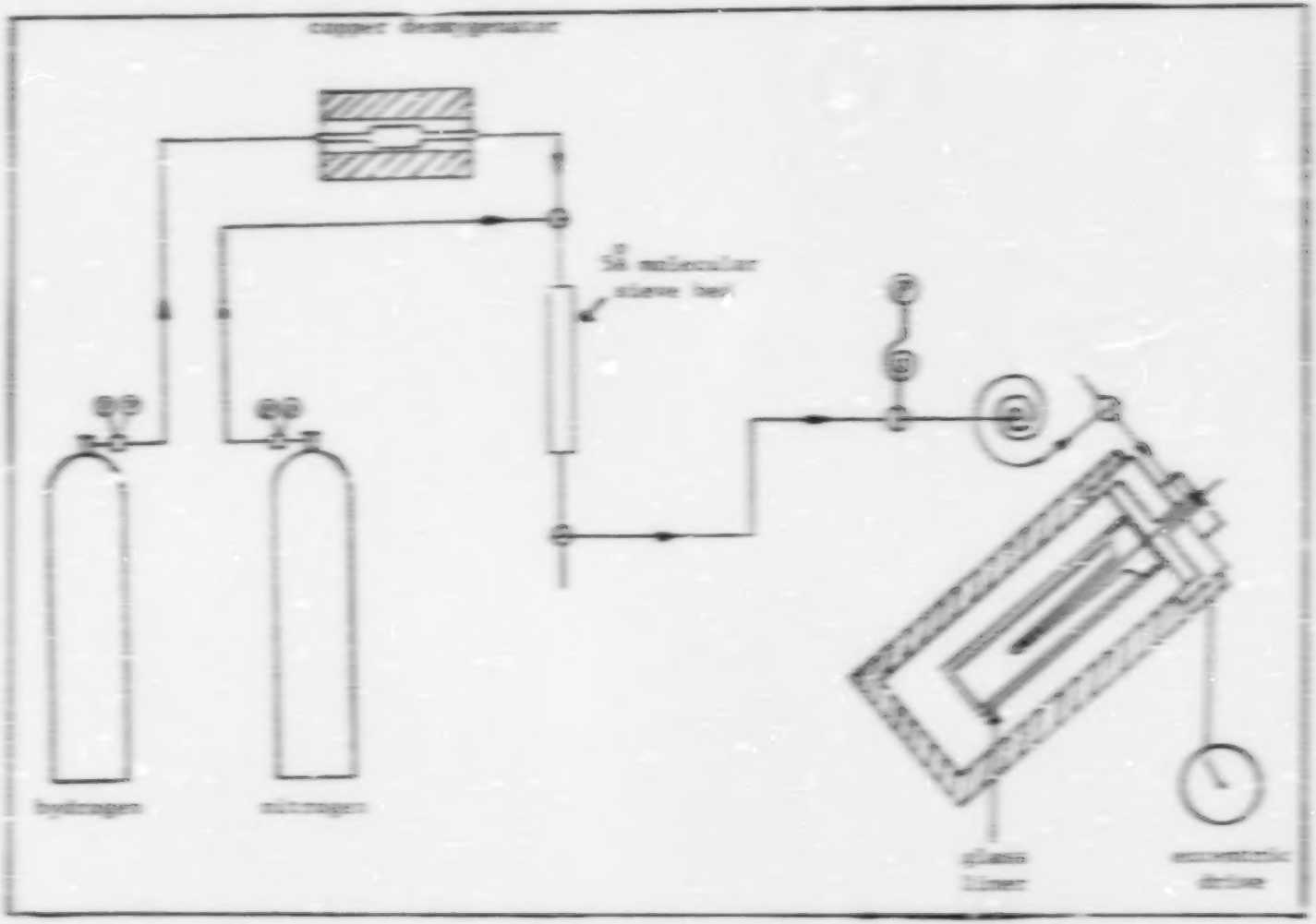


Figure 1. High pressure sorbing machine

SECTION 4

ANALYTICAL TECHNIQUES

GC-MS techniques were used for identification and quantitative analysis of all reactants and products studied during the course of these investigations on the hydrodechlorination of pesticides and related substances. The equipment used was a Perkin-Elmer 900 dual flame ionisation detector gas chromatograph interfaced with a DuPont 21-491 double focusing mass spectrometer. A CDI model 200 automatic digital integrator was used for quantifying FID output. Mass spectra were recorded using a CDI 5-124A recording oscillograph. Molecular weight determination and structural information obtained from the mass spectra of individual chromatographic peaks identified reaction intermediates in the complex systems studied. The FID response was found to be insensitive to chlorine content, thus allowing conversion and rate data to be obtained from comparison of the areas under the peaks on the chromatograms.

AROCLOR ANALYSIS

The total number of polychlorinated biphenyl compounds has been reported to be 210 (22, 23). Consequently, identification of each individual isomeric compound in an unknown sample was not practical. In this study, product compositions were quantified under two classifications. Firstly, unknowns were grouped under the number of chlorine atoms per molecule. Secondly, within each of these groups, products were further characterised by total ortho versus total (meta + para) substitution of chlorine. Gas chromatograph mass spectrometer analysis provided all the information necessary for the first determination (25, 26, 27). A chromatogram representative of this type of determination is given in Figure 6. The peaks, each of which is representative of a particular chlorinated biphenyl, are labled with the number of chlorine atoms contained in that molecule. The Aroclor 1248 used in this study was found to contain an average of 1.92 chlorine atoms per molecule and to have a molecular weight of 2892. Webb et al. (24) identified the major components of Aroclor 1221-1254 using gas chromatograph techniques. The quantification under chlorine substitution was obtained from the gas chromatograph data of this study by cross referencing with the published work of Webb.

1, 1-DIPHENYL ETHANES/ETHYLENES ANALYSIS (DDT, DDD, DDE)

Two different columns were used for analysis of chlorinated 1,1-diphenyl ethane/ethylene reactants and products. The mass spectra of a number of 2-chloro substituted 1,1-bis(p-chlorophenyl) ethanes and ethylenes have been reported (27, 28) and the spectra of corresponding hydrocarbons are available (29). However, mass spectra of reaction intermediates produced in

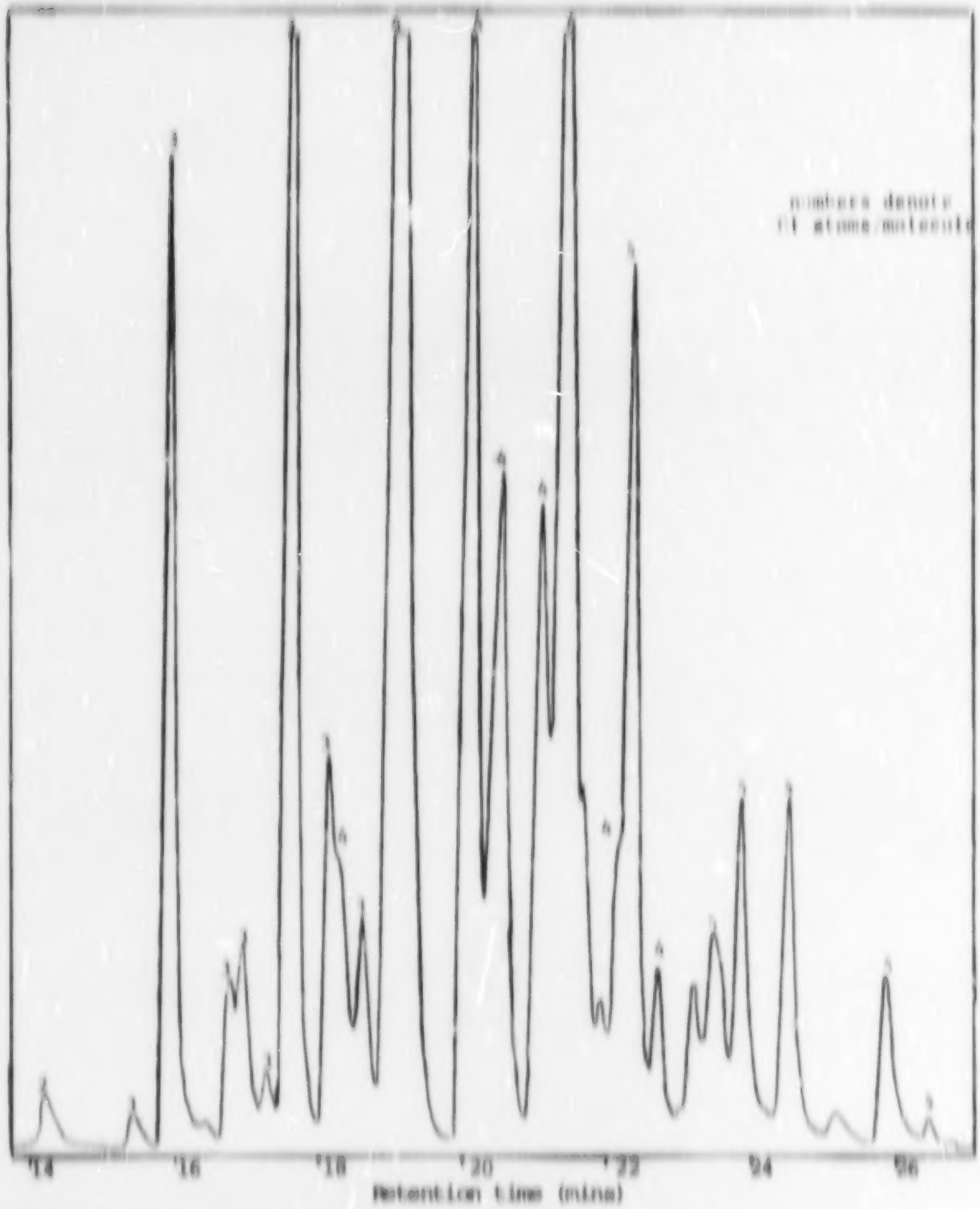
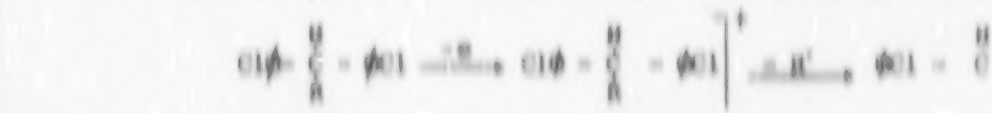


Figure 6. Aroclor 1248 chromatogram, 9'x1/8" 3% OV-17 on chromosorb W-HP, 122-250°C @ 5°C/min, He 30cc/min.

this study were not available. The process followed in developing these spectra and identifying the reaction products is outlined below.

ANALYSIS OF DDT AND DDE

The mass spectrometer fragmentation of every reported 1,1-bis (p-chlorophenyl) ethane is characterized by the following reaction:



Based on this information, similar behavior was proposed for reaction intermediates and this behavior was in fact observed. These reactions are displayed along with the relevant mass spectra in Figure 7. In addition to identification of the major fragmentation products, discrimination between products and reactants based on differences in aromatic chlorine content is thus obtained using the mass spectrometer. Differences in retention time in the gas chromatograph of reactants and products differing only in aliphatic (the R group above) chlorine content in conjunction with the observed mass spectra, allowed complete identification and quantification of the compounds involved in a given reaction.

ANALYSIS OF DDE

The mass spectra of chlorinated 1,1-diphenyl ethylene reactants and products reported in the literature (28, 29) and obtained in this study were analyzed. In all cases, fragmentation of the olefinic bond, which would be analogous to the initial reaction in the DDT MS analysis did not occur. This complicates the analysis, as the mass spectra obtained for DDE reaction intermediates containing the same number of chlorine atoms per molecule were similar. Compounds containing olefinic chlorine could not be distinguished from compounds containing aromatic chlorine based on mass spectra alone. Chromatographic retention time data was used to complete the identification with the exception that the identity of 1 and 2 chloro compounds were ambiguous.

ALDRIN AND DIELDRIN ANALYSIS

Partial identification of aldrin and dieldrin and their hydrochlorination products was carried out using the GLC/MS system. The mass spectrometer fragmentations of dieldrin and aldrin were characterized by retro-Diels-Alder(RDA) reactions (27) accompanied by expulsion of HCl or Cl as in the reaction:

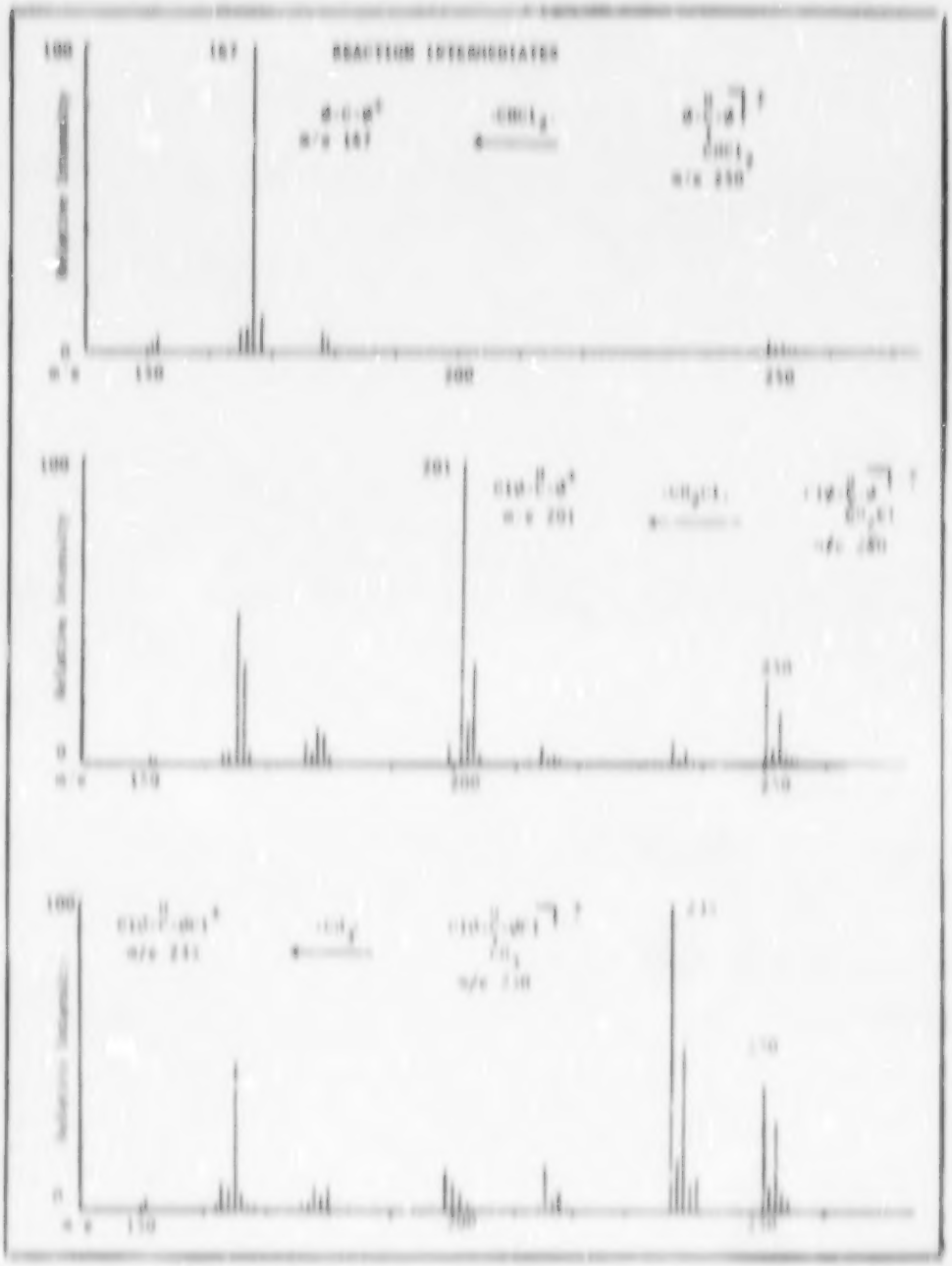


Figure 7. Representative mass spectra of (XX/XX)

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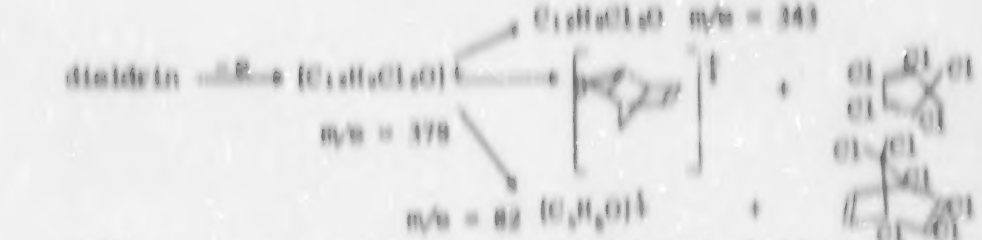
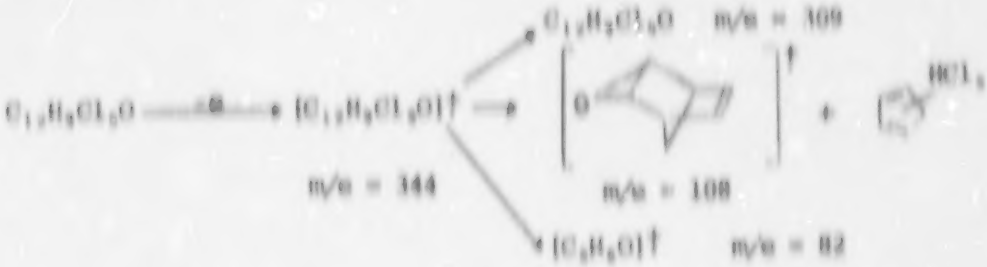


Similar spectra were obtained for dieldrin hydrodechlorination products according to the reaction:



Because these spectra were characterized by RDA reactions, no information could be obtained on which chlorine was removed during hydrodechlorination.

Mass spectra of aldrin, where one olefin had been saturated during hydrodechlorination, yielded more information, allowing further but not complete identification. The extent of analytic capability is indicated in Table 1 for aldrin and in Table 2 for dieldrin.

TOXAPHENE ANALYSIS

Toxaphene is a complex mixture of polychlorinated camphene isomers. Toxaphene and its hydrodechlorination products were analyzed using GC-MS techniques. Mass spectra have been reported (10) for toxaphene and analyzed (11) in conjunction with the data of this study. The determination illustrated in the chromatogram of Figure 8 is at best qualitative.

TOXICOLOGY

As a part of this study, EPA arranged that starting materials and products used in this study would be examined for toxicity by the Toxicology Division, Biomedical Laboratory, Edgewood Arsenal. The LD_{50} of the test solution was injected intravenously into the tails of white mice. Some of the test results are reported as preliminary, while others show that the solvent (hexane) is more toxic than the pesticide. It was not possible to distinguish between the starting materials and ordinary acceptable chemicals (i.e. solvents used) using the techniques employed. Therefore, the use of this toxicity test data for assessment of environmental acceptability of material used in this study was not recommended by the researchers.

TABLE 1. RETENTION TIMES FOR MAJOR ALDRIN PRODUCTS

(9' x 1/8" 3% OV-17 on chromosorb W-HP 102-250°C @ 8°C/min 30 cc/min He)

R.T. (min)	MS IDENTIFICATION
10.6	$C_{12}H_{10}Cl_2$
14.1	$C_{12}H_{11}Cl_3$
15.1	$C_{12}H_{12}Cl_4$
15.6	$C_{12}H_8Cl_6$ (ALDRIN)
16.2	$C_{12}H_{11}Cl_5$
16.4	$C_{12}H_{10}Cl_6$

TABLE 2. RETENTION TIMES FOR MAJOR DIELDRIN PRODUCTS

(9' x 1/8" 3% OV-17 on chromosorb W-HP 102-250°C @ 8°C/min 30 cc/min He)

R.T. (min)	MS IDENTIFICATION
18.0	$C_{12}H_{10}Cl_6O$
18.4	$C_{12}H_8Cl_6O$ (DIELDRIN) + $C_{12}H_8Cl_6O$

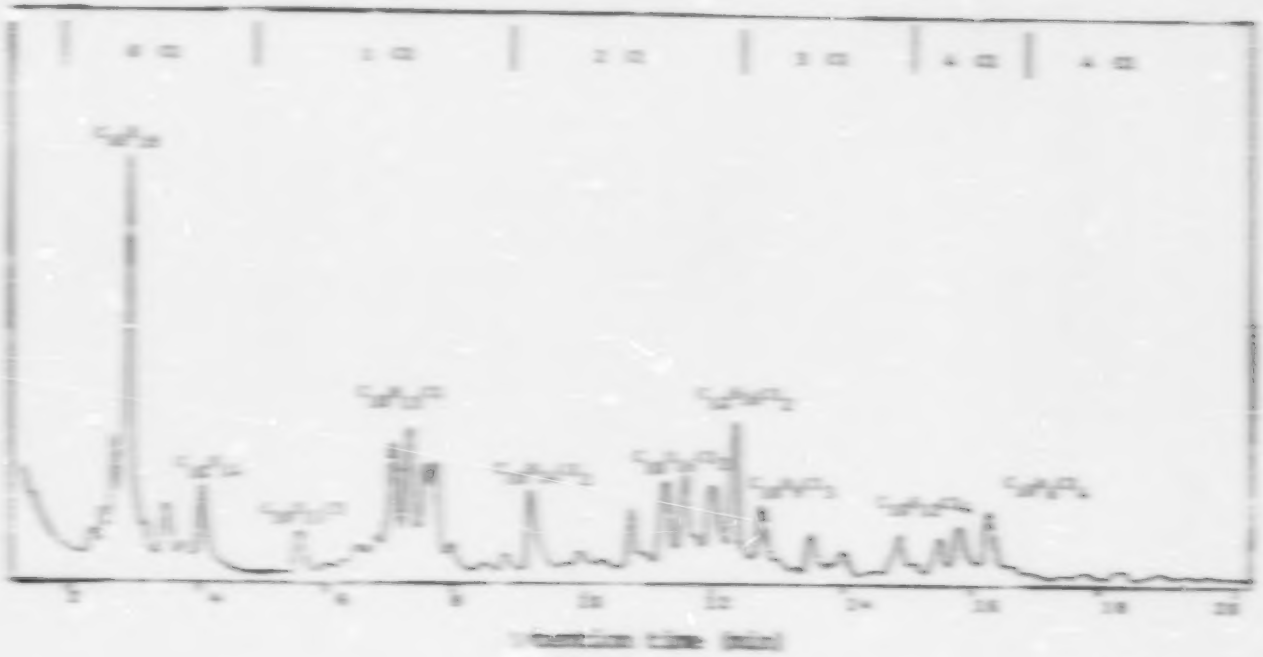


Figure 6. [illegible] GC/MS analysis of complex hydrodechlorination products. [illegible] in [illegible] on chromosorb W-HP, 60-250°C @ 8°C/min.

SECTION 5

RESULTS

ARACLOR 1248

Aroclor 1248, a clear viscous oil containing 48 wt% chlorine, was the polychlorinated biphenyl (PCB) used as the model reaction mixture. Three sets of experiments were conducted using Aroclor 1248. Firstly, the pulsed microreactor was used to verify reactivity of the volatilised PCB in the presence of the Pd catalyst. Secondly, preliminary experiments in the teflon lined autoclave established the reactivity in the liquid phase using the Pd catalyst. Thirdly, continuous sampling experiments in the teflon lined autoclave provided data for rate and selectivity analysis. Chlorine conversion, X, is used as the indicator of extent of reaction and is defined as:

$$X = 1 - \frac{\sum_{i=0}^{n} i\phi_i^t}{\sum_{i=0}^{n} i\phi_i^0}$$

where ϕ_i^t is the percentage of biphenyl containing i chlorine atoms per molecule, and ϕ_i^0 is the initial percent of a given molecule containing i chlorine atoms.

1. One Phase Pulsed Microreactor Screening

Four experiments were conducted at the same temperature (220°C), pressure (2.1 atm H_2), space time (10^{-3} seconds), and feed composition (0.7 wt% Aroclor in n-heptane). The concentrations of Pd catalyst on 5m^2/g of Al_2O_3 support were varied. These experiments demonstrated the feasibility of catalytic hydrodechlorination of Aroclor 1248. The results are presented in Table 1. A semi-log plot of (1-x) versus g Pd indicates that the chlorine conversion approximates first order behavior in Pd.

TABLE 1. PULSE MICROREACTOR ARACLOR 1248 HYDRODECHLORINATION

220°C 2.3 ATM H_2	τ = .01 sec.			
Catalyst wt (mg)	5.0	4.6	5.0	5.0
wt % Pd	.00	.05	.10	.35
ϕ_0:	---	.134	.296	.758
ϕ_1:	.003	.058	.068	.043
ϕ_2:	.013	.129	.140	.094
ϕ_3:	.305	.337	.279	.070
ϕ_4:	.493	.236	.166	.026
ϕ_5:	.189	.091	.046	---
X	.013	.304	.469	.855

2. Preliminary Liquid Phase Experiments

In these experiments the teflon-lined autoclave was initially charged with Aroclor in ethanol using 61% Ni on kieselguhr as catalyst, and with the acid acceptor, NaOH. The reactor was then heated, pressurized with H_2, maintained near these conditions for the reaction time, and finally cooled. The contents were analyzed at this final condition. Temperature, H_2 pressure, reaction time, and ratio of weight of reactant to weight of catalyst were varied. The conditions and results are summarized in Table 4. The following conclusions were drawn from this set of experiments:

1) Complete hydrodechlorination of PCB can be obtained using Ni catalyst at elevated H_2 pressure (50 atm) and temperature (115°C) in a six hour reaction period.

2) The reaction has positive dependence on H_2 pressure above 25 atmospheres.

3) Catalyst poisoning occurs at 175°C placing an upper limit on reaction temperature.

3. Continuous Sampling Liquid Phase Experiments

Experiments were conducted at four temperatures (60°, 80°, 100°, 130°C) in the teflon-lined autoclave. In each experiment, the H_2 pressure (50 atm), catalyst (Ni), acid acceptor (NaOH), and initial reactant composition (2 wt% Aroclor in ethanol) were reproduced. Samples were withdrawn and analyzed at

| | | |

intervals during the reaction. Selectivity data are plotted versus chlorine conversion in Figures 9, 10 and 11. Selectivity data obtained at these four temperatures were sufficiently similar that they were treated as one set of data. Two models were developed to interpret the reaction results.

(a) Consecutive Reaction Scheme

The observed selectivity data were fitted to a consecutive reaction

$$\phi\phi_1 \xrightarrow{k_{11}} \phi\phi_2 \xrightarrow{k_{12}} \phi\phi_3 \xrightarrow{k_{13}} \phi\phi_4 \xrightarrow{k_{14}} \phi\phi_5 \xrightarrow{k_{15}} \phi\phi_6$$

scheme described by a set of first order reaction path expressions.

$$\frac{\phi\phi_1}{\phi\phi_1} = \frac{k_{11}}{k_{11}} \frac{\phi\phi_1}{\phi\phi_1} = 1$$

$$\frac{\phi\phi_2}{\phi\phi_1} = \frac{k_{12}\phi\phi_2 - k_{11}\phi\phi_1}{k_{11}\phi\phi_1}$$

$$\frac{\phi\phi_3}{\phi\phi_1} = \frac{k_{13}\phi\phi_3 - k_{12}\phi\phi_2}{k_{11}\phi\phi_1}$$

$$\frac{\phi\phi_4}{\phi\phi_1} = \frac{k_{14}\phi\phi_4 - k_{13}\phi\phi_3}{k_{11}\phi\phi_1}$$

$$\frac{\phi\phi_5}{\phi\phi_1} = \frac{k_{15}\phi\phi_5}{k_{11}\phi\phi_1}$$

The best fit was obtained with the following set of relative rate constants.

$\frac{k_{12}}{k_{11}}$	$\frac{k_{13}}{k_{11}}$	$\frac{k_{14}}{k_{11}}$	$\frac{k_{15}}{k_{11}}$
0.40	0.23	0.36	0.40

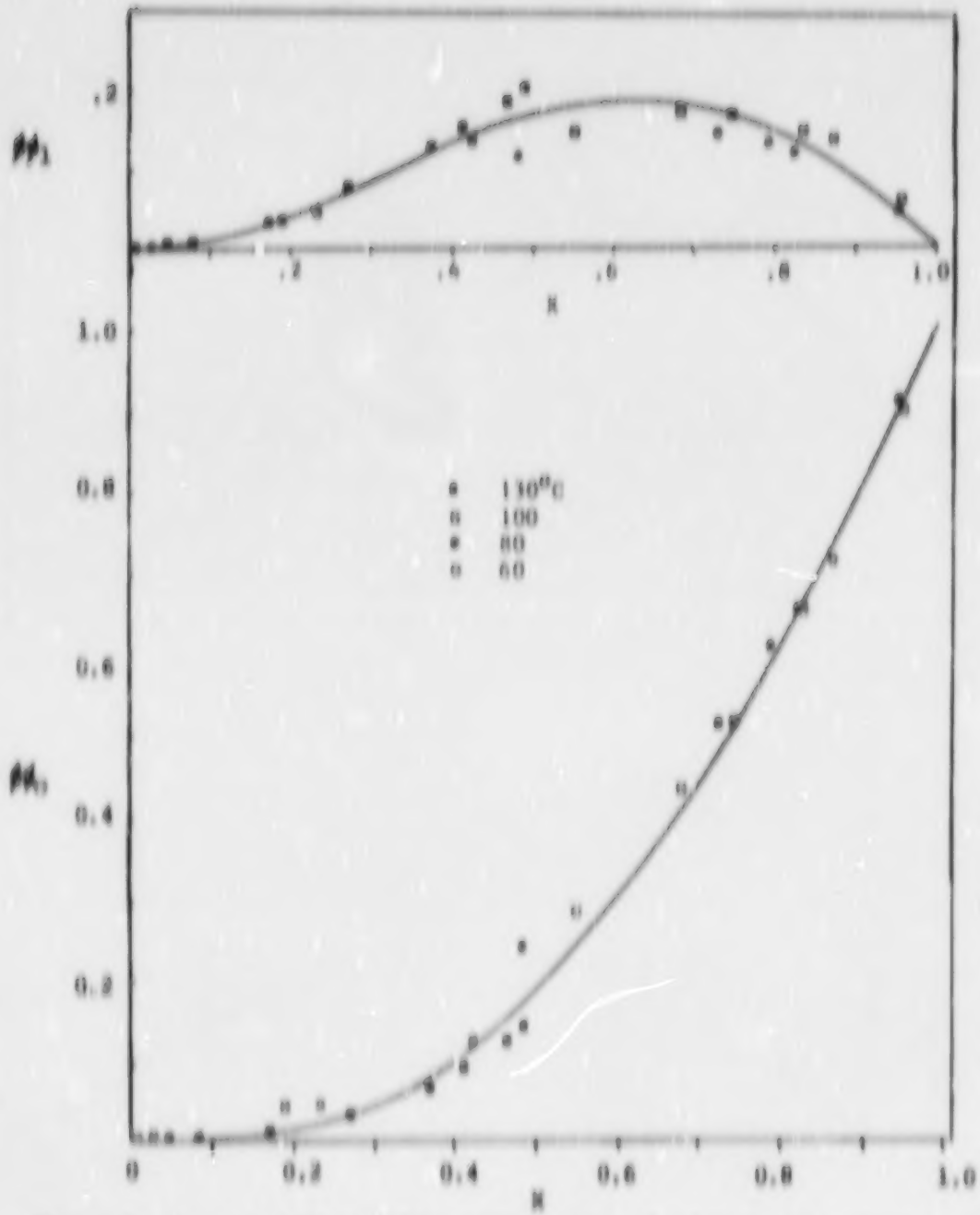


Figure 9. Aerolite 1348 relative product distribution data(50 atm.H_2, Ni in kiomoles/hr).

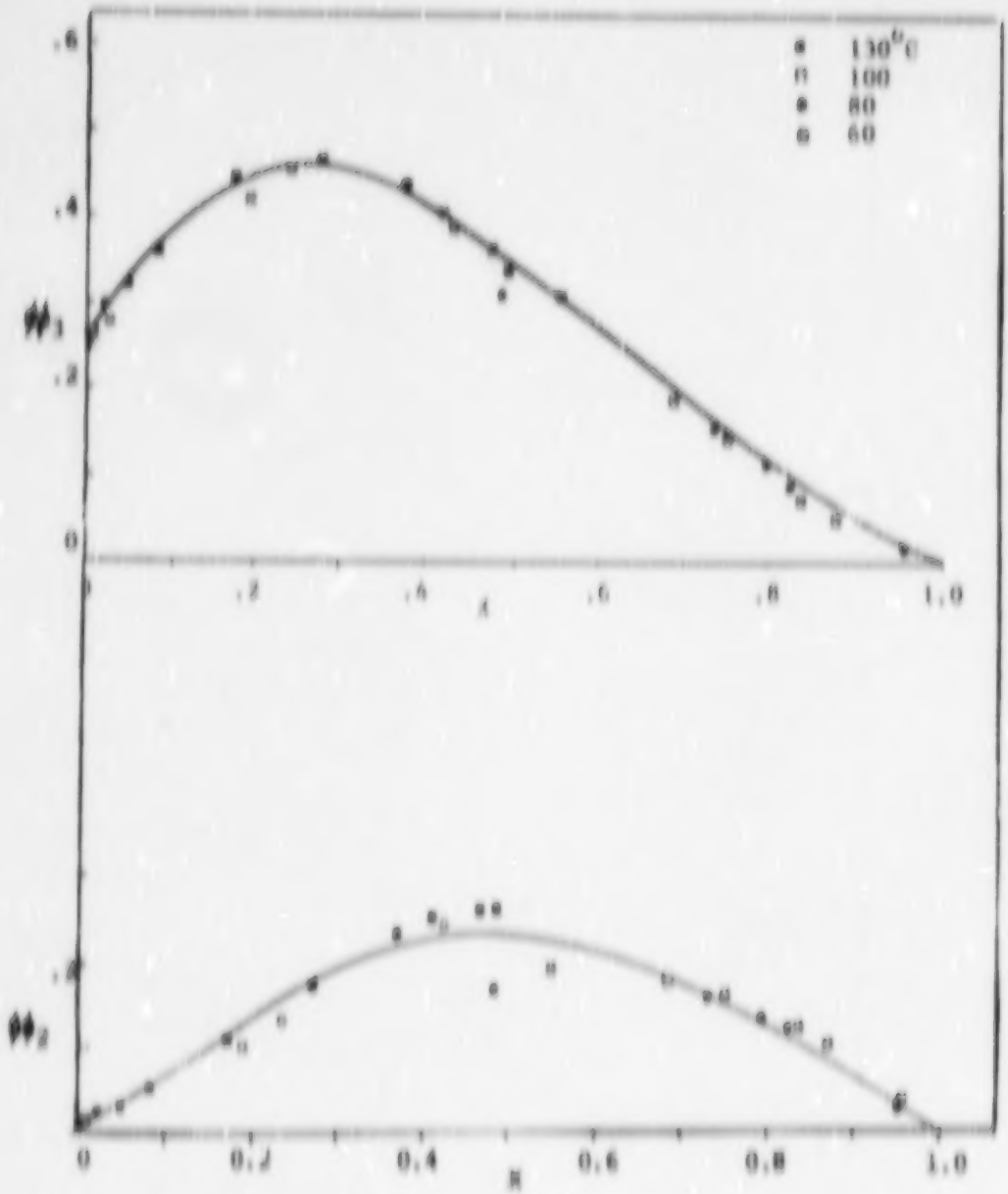


Figure 10. Arrelon 1268 relative product distribution data (50 atm.H_2, 80 cm blowsignal).

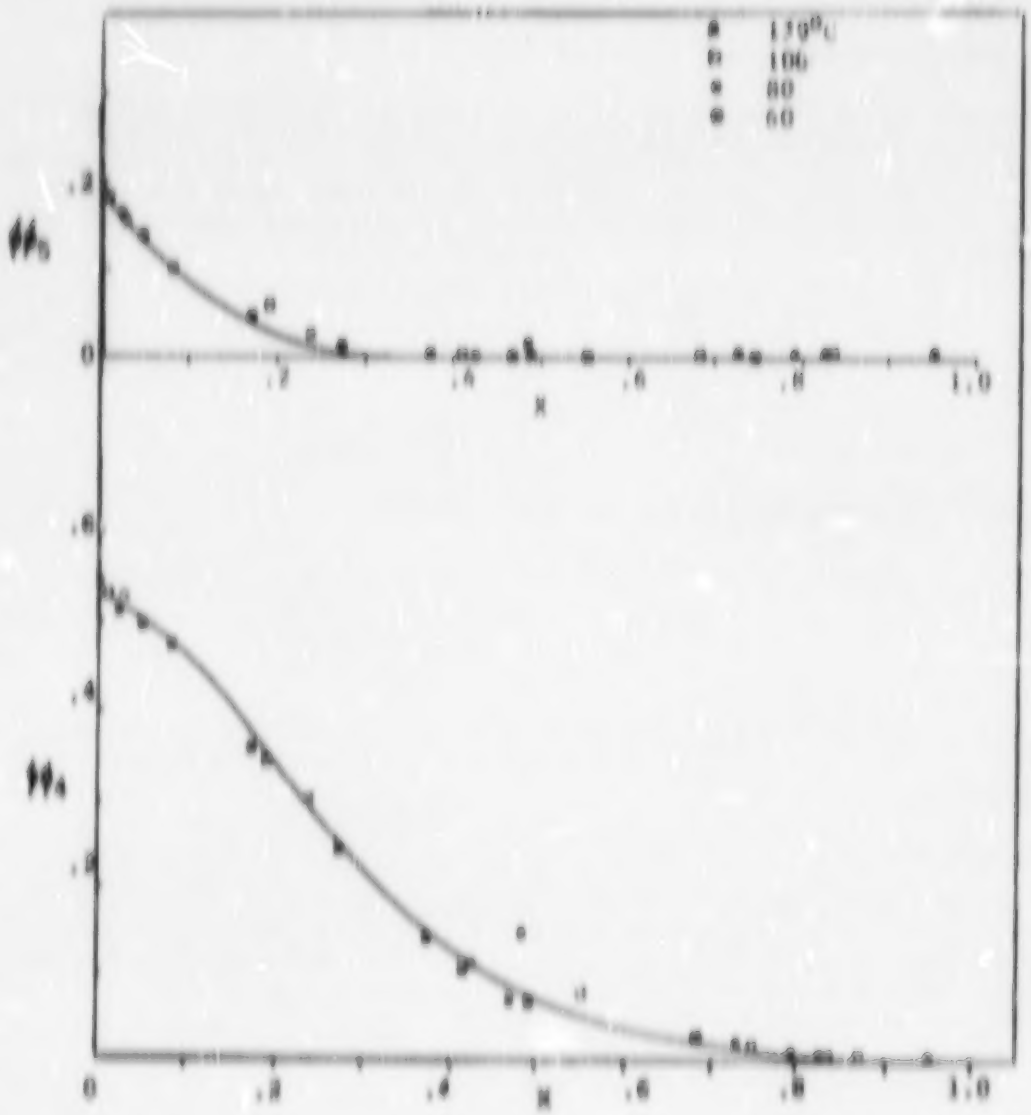


Figure 11. Aroclor 1248 relative product distribution data (50 atm. H_2, Ni on kieselguhr).

The curves obtained using this set of constants are superimposed on the data in Figures 9, 10 and 11. A semi-log plot of (1-X) versus time for data is given in Figure 12. An analogous plot obtained from the model would be curves and consequently in disagreement with the data. A Langmuir Hinshelwood kinetic model which takes into account adsorption effects ,covided insight into this problem.

(b) Relative Rates of Isomeric Reactions

In the course of these studies it was observed that, within each group of PCB isomers containing the same number of chlorine atoms per molecule, certain isomers were selectively produced and reacted. In all cases, during a reaction the amount of ortho substituted isomers increased relative to the amount of meta and para isomers present. First order rate expressions were proposed.

$$\frac{dO}{dt} = k_O^0$$

$$\frac{d(\quad)}{dt} = k_{m,p} \quad M'$$

Dividing these expressions and integrating gives:

$$\frac{\log \frac{O}{O_0}}{\log \frac{M'}{M'_0}} = \frac{k_O}{k_{m,p}}$$

A log-log plot (Figure 13) fits a straight line as predicted by the model. A differing slope for the 130°C experiment is indicative of catalyst deactivation.

(HP, HH, HB)

Three reactors were used in this portion of the study. The pulsed microreactor was used to screen for the thermal and catalytic reactivity of HP and HH. The continuous gas phase reactor was used to hydrodechlorinate HB and HH. The teflon-lined autoclave was used in a series of dechlorinated reactions involving HP and HH.

1. Gas Phase Pulsed Microreactor Experiments

The three sets of experiments conducted in this reactor established the reactivity of catalytic hydrodechlorination of HP, HH, and HH.

a) Using no catalyst and no hydrogen and with helium as the carrier gas, it was found that 0.5 µl samples of 9.5 wt% HP in p-xylene underwent thermal decomposition over a range of temperatures (200-360°C). HH was the major reaction product.

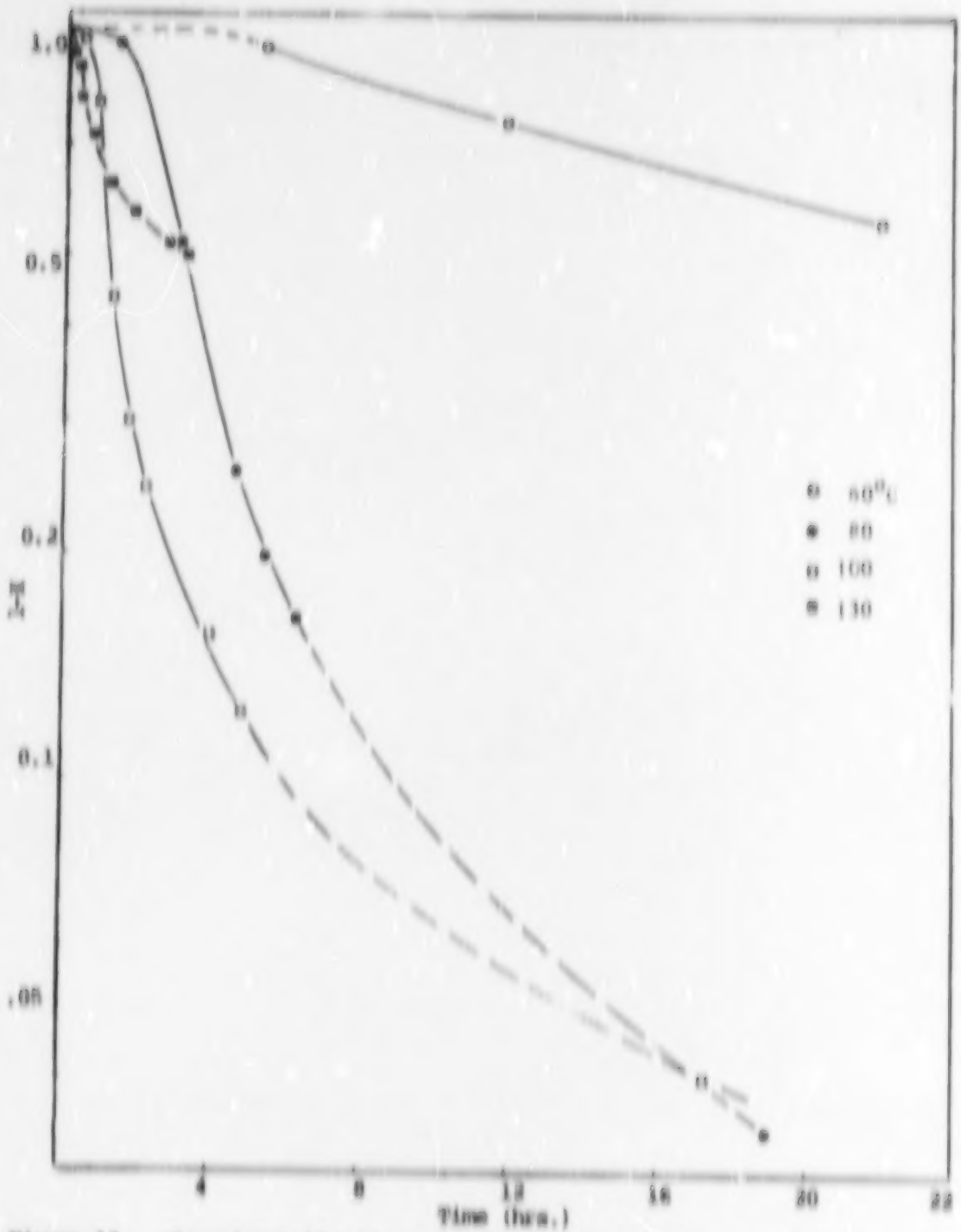


Figure 12. Experimentally observed Aroclor 1248 kinetics.

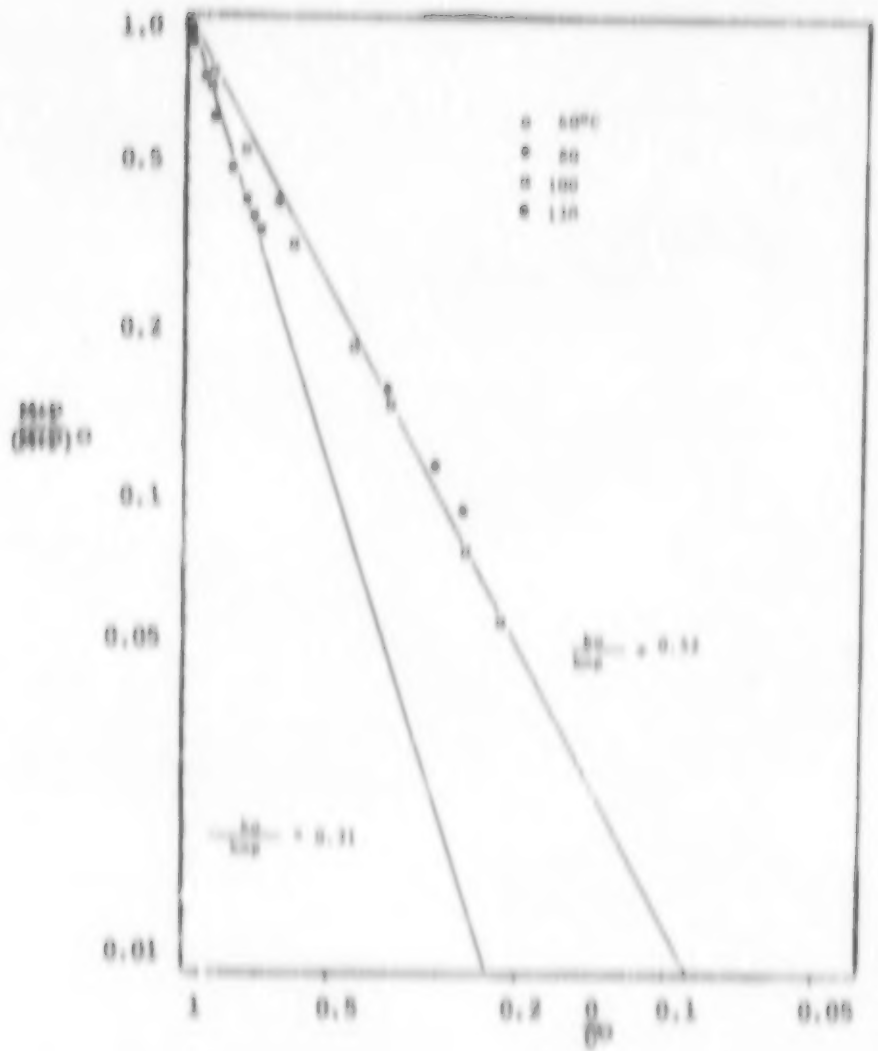


Figure 13. Acrylic 1248 hydrodechlorination as characterized by β^{-} vs. (m/g) substitution.

b) A set of six experiments was conducted using 0.5 µl samples of 5.2 wt% DMT at a pressure of 2.3 atm, a temperature of 220°C, and a space time of .01 seconds. The first two experiments investigated thermal reactions in the empty reactor with He and H_2 as the carrier gases. The remaining four experiments were conducted with H_2 carrier gas, Al_2O_3 support, and varying concentrations (0.0, 0.05, 0.10, 0.35 wt%) of Pd catalyst. Chromatograms for the products of these experiments are presented in Figure 14. The results show that the thermal reaction was minimal but that Al_2O_3(no Pd) catalysed hydrodechlorination of the aliphatic part of DMT, with DMB as the major reaction product. Aromatic hydrodechlorination was affected only with Pd present.

c) This set of six experiments was identical to set (b) with the exception that 0.5µl samples of 5.1 wt% DMB were injected. The results, presented in Figure 15, show that the thermal reaction was minimal, that the hydrodechlorination catalysed by Al_2O_3 occurred to a lesser extent than with DMT, and that DMB was generally less reactive than DMT with Pd catalyst present.

(2) Continuous Gas Phase Reactor Experiments

(a) DMB

In a single experiment, the rate of DMB hydrodechlorination at a temperature of 220°C and hydrogen partial pressure of 65 ± 5 mm Hg was measured by varying DMB partial pressure from 0.214 mm Hg to 0.529 mm Hg, and by varying space time from 0.0582 seconds to 0.0674 seconds. It was found that the initial reaction, which is diagrammed in Figure 16 along with the data, occurred in a single step without intermediate desorption.

(b) DMT

The following three sets of experiments were conducted in the continuous gas phase reactor with DMT as reactant:

i) An experiment, conducted at 300°C, hydrogen partial pressure of 555 mm Hg, DMT partial pressure of 0.688 mm Hg, space time of 0.0482 seconds, and with 0.35 wt% Pd on Al_2O_3 catalyst, demonstrated that catalyst activity declined rapidly during the first 24 hours of a run, but stabilized thereafter. All kinetic data was taken after the catalyst had been on stream for more than one day.

ii) In an experiment conducted at conditions identical to experiment (i) above, with the exception that no Pd was present, it was found that Al_2O_3 did not catalyse hydrodechlorination of DMT. This result differed from that obtained in the pulsed microreactor.

iii) In a series of five experiments conducted at three temperatures and three partial pressures of hydrogen, rate and

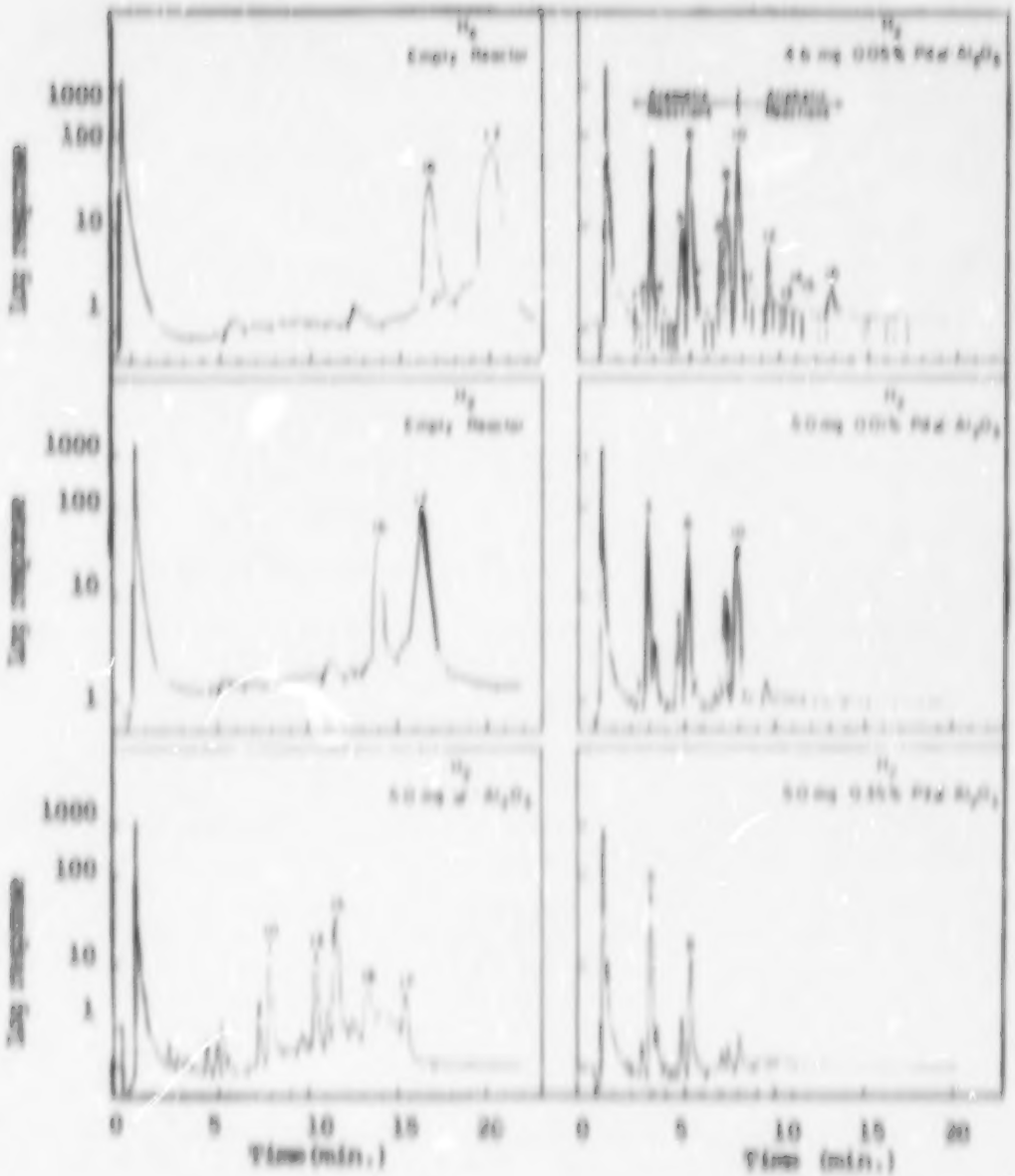


Figure 14. IBT hydrocarbonization
(30 cm³/min.gas, 220*10⁵ N/m², 15 min).

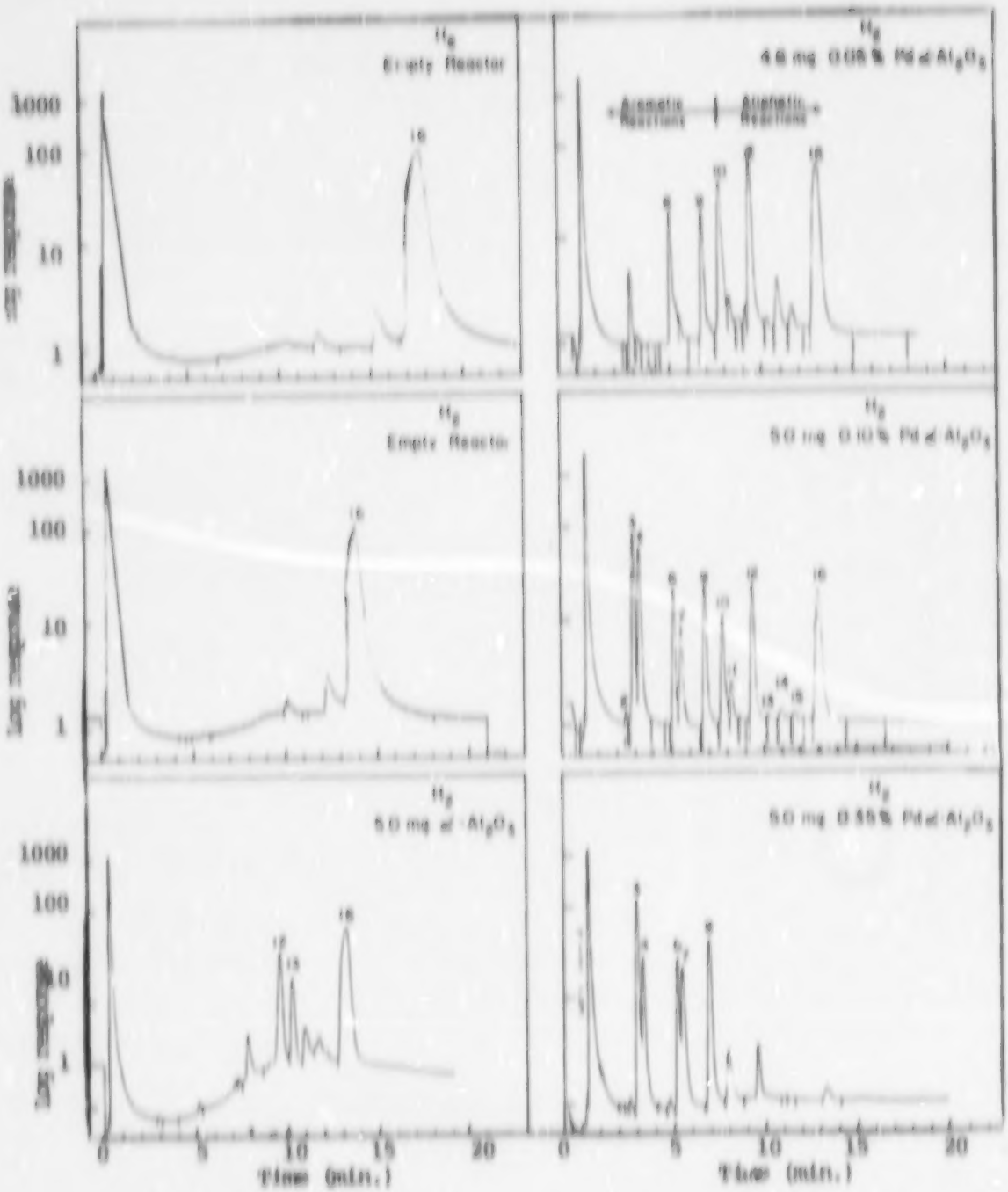


Figure 15. (RR) hydrocondensation
(30 sccm/min. gas, 225° 5°C, 19 psig).

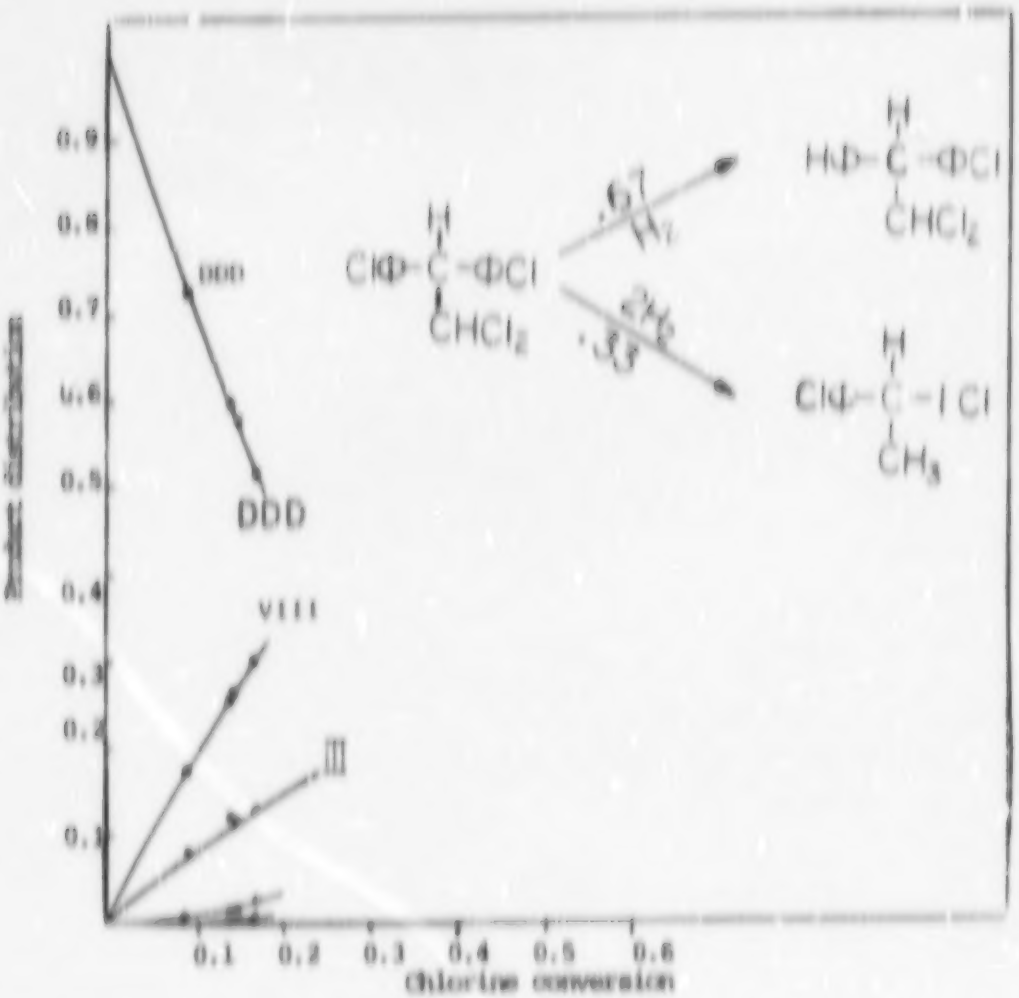


Figure 16. DDD Selectivity Plot

selectivity data were obtained by varying space time and DDE partial pressure. Five major DDE (species VI) hydrodechlorination products were observed. These compounds, which amounted to 95% of the total products, are labeled with Roman numerals in the following list:

1,1-diphenylethane	$\phi-\underset{\underset{CH_3}{|}}{\overset{\overset{H}{|}}{C}}-\phi$	I
1-chlorophenyl,1-phenylethane	$Cl\phi-\underset{\underset{CH_3}{|}}{\overset{\overset{H}{|}}{C}}-\phi$	II
1,1-bis-parachlorophenylethane	$Cl\phi-\underset{\underset{CH_3}{|}}{\overset{\overset{H}{|}}{C}}-\phi Cl$	III
1,1-diphenylethylene dichloride	$\phi-\underset{\underset{CCl_2}{\|}}{C}-\phi$	IV
1-chlorophenyl,1-phenylethylene dichloride	$\phi-\underset{\underset{CCl_2}{\|}}{C}-\phi Cl$	V

Chlorine conversion was used as an extent-of-reaction parameter and is defined as $\frac{\phi_O-\phi}{\phi_O}$, where $\phi=\sum_{i=0}^{i=4} iCl_i$, ϕ_O is 4, based on the chlorine content of starting material, i=number of chlorines per molecule, and Cl_i = mole fraction of compounds having i chlorines per molecule. Representative selectivity data along with temperature and pressure conditions at which they were obtained are presented in Figures 17 and 18. The solid curves and reaction constants are a computer fit of the data calculated from the reaction path model represented above the curves. The complete reaction scheme suggested by the data is as follows:

The following three assumptions were employed in the modelling:

1) The reactor is back-mixed. This assumption is supported by the relatively high value of the vessel dispersion number. 2) Langmuir Hinshelwood kinetics describe the reaction system. 3) First order functionality represents the rates. The rates were:

$$r_{VI} = -(k_{65} + k_{63})\ VI$$

$$r_{V} = k_{65}\ VI - (k_{54} + k_{52})\ V$$

$$r_{IV} = k_{54}\ V - k_{41}\ IV$$

$$r_{III} = k_{63}\ VI - k_{32}\ III$$

$$r_{II} = k_{32}\ III + k_{52}\ V - k_{11}\ II$$

$$r_{I} = k_{21}\ II + k_{41}\ IV$$

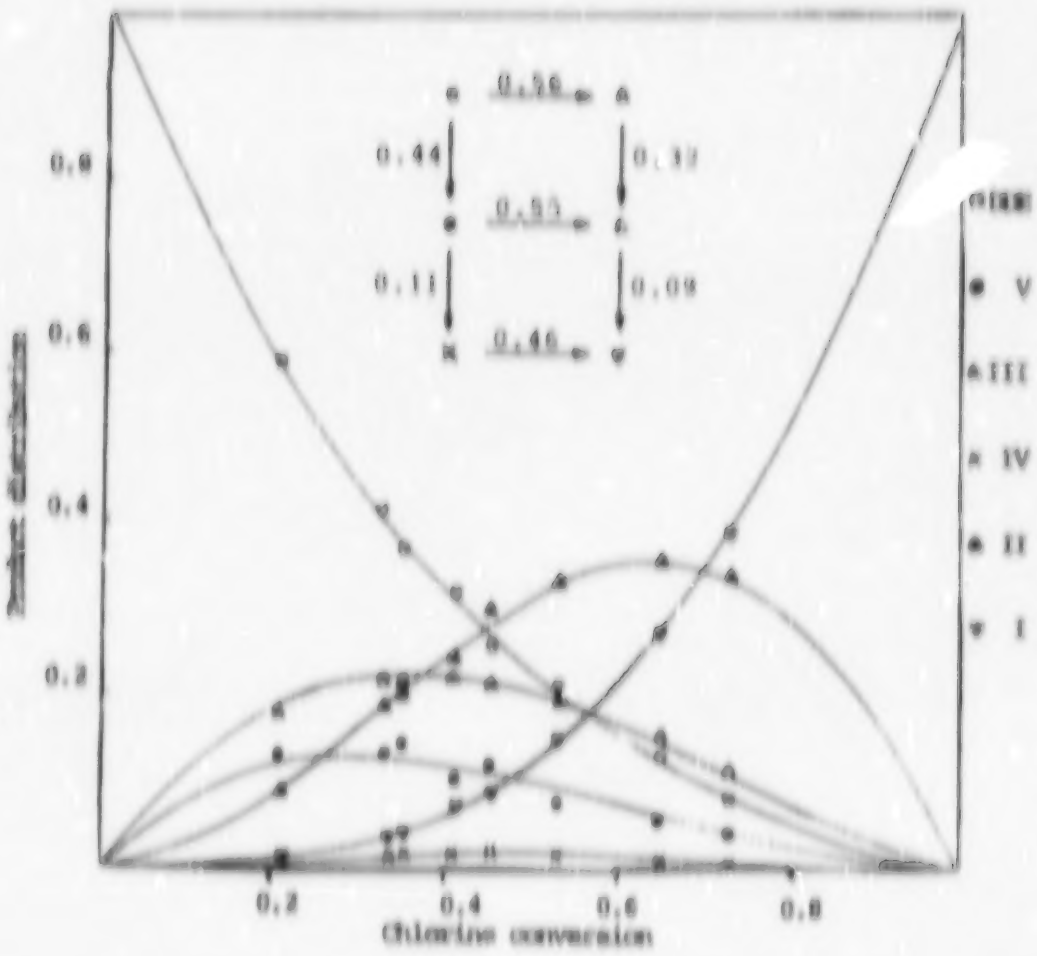


Figure 17. IIR Selectivity Plot (A)
(T=200°C, P_{H_2} = 140 ± 30mm. Hg)

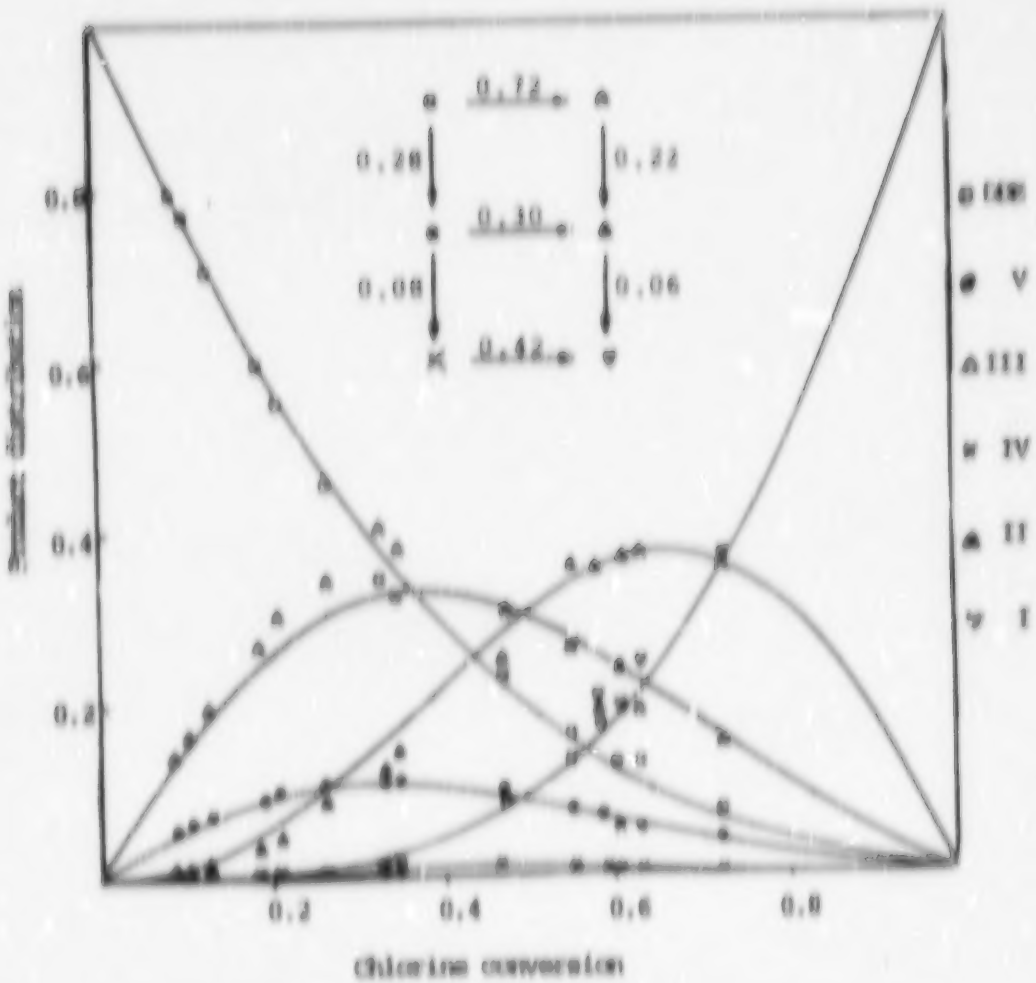


Figure 18. [illegible] selectivity plot (B)
(T=200°C; P_{H_2} = 580-90 mm.Hg).

Define relative rates:

$$r_V^0 = \frac{r_V}{[V]_1} \; ; \; r_{IV}^0 = \frac{r_{IV}}{[V]_1} \; , \; r_{III}^0 = \frac{r_{III}}{[V]_1} \; , \; r_{II}^0 = \frac{r_{II}}{[V]_1} \; , \; r_I^0 = \frac{r_I}{[V]_1}$$

and $$V^0 = \frac{V}{[V]_1} \; , \quad IV^0 = \frac{IV}{[V]_1} \; , \quad III^0 = \frac{III}{[V]_1} \; , \quad II^0 = \frac{II}{[V]_1} \; , \quad I^0 = \frac{I}{[V]_1}$$

Also define relative rate constants:

$$a = \frac{k_{65}}{k_{65}+k_{63}} \qquad d = \frac{k_{63}}{k_{65}+k_{63}} \qquad b = \frac{k_{52}}{k_{65}+k_{63}} \qquad e = \frac{k_{32}}{k_{65}+k_{63}}$$

$$c = \frac{k_{54}}{k_{65}+k_{63}} \qquad g = \frac{k_{21}}{k_{65}+k_{63}} \qquad f = \frac{k_{41}}{k_{65}+k_{63}}$$

then:

$$r_V^0 = a - (b + c)\, V^0$$

$$r_{III}^0 = d - e\, III^0$$

$$r_{IV}^0 = cV^0 - IV^0$$

$$r_{II}^0 = eIII^0 + bV^0 - gII^0$$

$$r_I^0 = IV^0 + gII^0 \qquad \text{and } a + d = 1$$

Rate constants defined above relative to $(k_{65}+k_{63})$ were matched with experimental results.

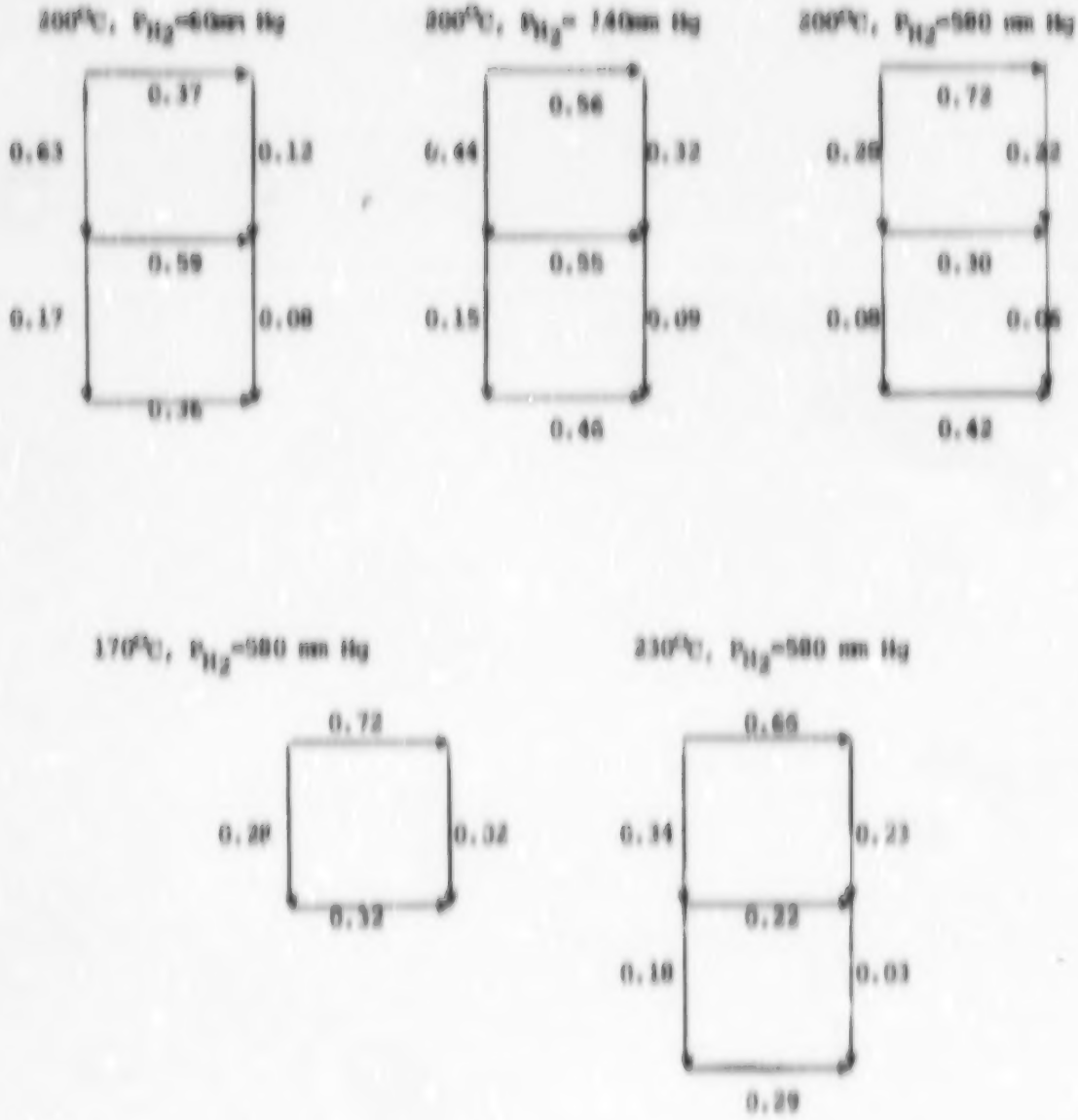


Figure 19. IRE relative rate constants
(0.35% Pd on γ- Al_2O_3)

Temperature changes did not appreciably affect the relative rates of olefinic and aromatic hydrodechlorination at constant temperatures. If it is assumed that olefinic hydrodechlorination is of order n with respect to H_2 partial pressure and aromatic hydrodechlorination is of order m with respect to H_2 partial pressure, it can be shown that the relative rate constants of olefinic reaction decreases as H_2 partial pressure decreases. The same trend is demonstrated by a Langmuir Hinshelwood model based on dissociative adsorption of hydrogen and bimolecular surface reaction of DDE with hydrogen. Correlations, based on assumptions regarding the relative sizes of equilibrium adsorption constants, demonstrated that the rate of hydrodechlorination of DDE increases linearly with the product of DDE partial pressure and the square root of the H_2 partial pressure. Similar correlations demonstrated that the rate of removal of aromatic chlorine and of olefinic chlorine from DDE should be linearly proportionate to the product of DDE partial pressure, and a function of the hydrogen partial pressure. For aromatic chlorine, this function was the square root of the partial pressure of hydrogen; while for olefinic chlorine the function was the partial pressure of hydrogen.

An additional result of these experiments is the following reactivity sequence. Initial hydrogenation of DDE did not occur and the fact that only trace olefinic intermediates were observed may indicate the existence of a non-equilibrium adsorption-desorption sequence. A comparison of DDD and DDE reactions conducted at similar conditions used in conjunction with the fact that olefinic chlorines are more reactive than aromatic chlorines, gives the following reactivity order for hydrodechlorination in the DDD, DDE sequence. In the DDD, DDE sequence:

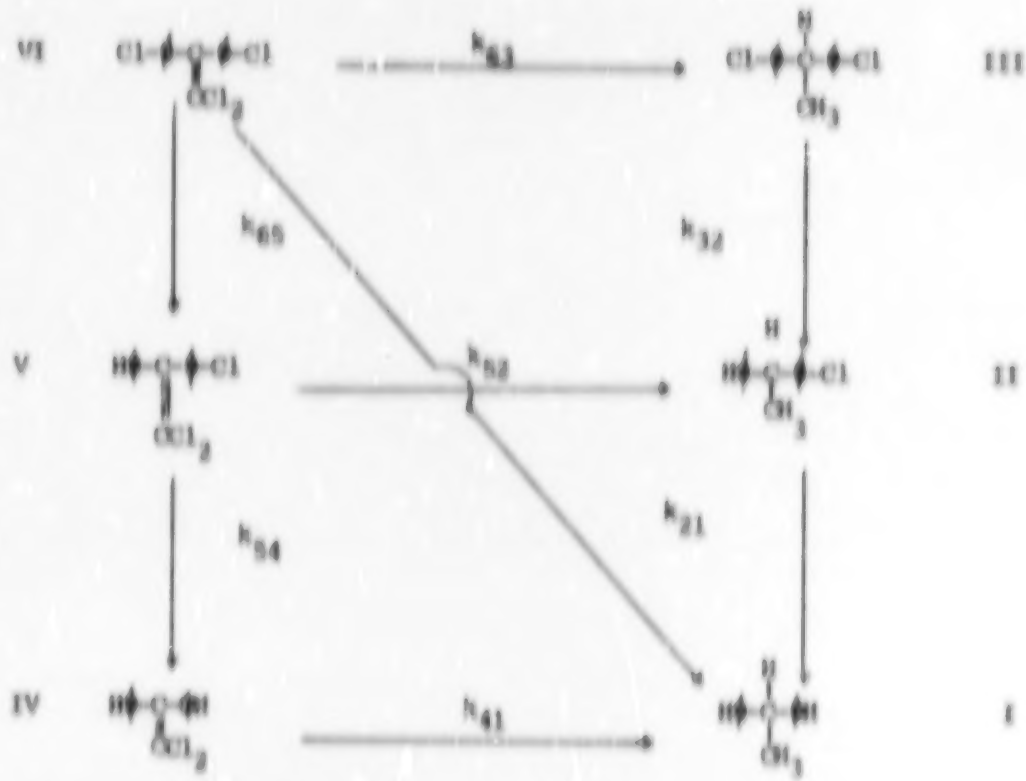
3. Liquid Phase Reactions in the Teflon Lined Autoclave

A preliminary experiment was conducted with DDT in the teflon-lined autoclave to determine if a hydrocarbon solvent, xylene, and the acid acceptor $Ca(OH)_2$ could be used in the liquid phase hydrodechlorination process with Ni catalyst. Only trace amounts of the desired product were formed, indicating that the acid acceptor should be soluble in the reaction mixture and that ethanol as solvent is favored over xylene.

A more complete set of experiments using ethanol solvent and Pd and Ni catalyst were carried out in the teflon-lined autoclave to investigate: 1) liquid phase stoichiometry; 2) reaction paths and associated rate constants; 3) the effects of catalyst loading and stirrer speed on reaction rate; and 4) the effect of hydrogen pressure and temperature on rates and selectivity in DDE hydrodechlorination. Conditions for these experiments are summarized in Table 5.

(i) Liquid Phase Stoichiometry

Similarly to the gas phase reaction, both Ni and Pd catalysed consecutive removal of both olefinic chlorines in the liquid phase reaction. (III) was not observed, indicating that olefinic hydrodechlorination precedes olefinic hydrogenation. The major difference between gas and liquid phase hydrodechlorination of (III) was that concerted or simultaneous removal of aromatic and olefinic chlorines occurred in the liquid phase reaction. The overall stoichiometry for liquid phase hydrodechlorination of (III) is characterized as:



(ii) Reaction Paths

Similar to the treatment described for Aroclor 1248, (III) hydrodechlorination stoichiometry can be described by a set of normalised first order differential equations which simulate batch reaction behavior.

$$\frac{d\,V}{d\,VI} = \frac{k_{65}VI - (k_{52} + k_{54})\,V}{-(k_{51} + k_{56} + k_{52} + k_{54})\,VI}$$

$$\frac{d\,IV}{d\,VI} = \frac{k_{54}V - k_{41}IV}{-(k_{51} + k_{56} + k_{52} + k_{54})\,VI}$$

$$\frac{d\,III}{d\,VI} = \frac{k_{63}VI - k_{32}III}{-(k_{51} + k_{56} + k_{52} + k_{54})VI}$$

$$\frac{d\,II}{d\,VI} = \frac{k_{52}VI + k_{32}III - k_{21}II}{-(k_{51} + k_{56} + k_{52} + k_{54})VI}$$

$$\frac{d\,I}{d\,VI} = \frac{k_{51}VI + k_{21}II + k_{41}IV}{-(k_{51} + k_{56} + k_{52} + k_{54})VI}$$

There is no unique solution to this set of equations. However, simplifying assumptions can be applied to yield unique solutions. The results obtained through this approach are drawn over representative Figures 20 and 21. With the values of the relative rate constants obtained, it is possible to determine the total initial olefinic and aromatic hydrochlorination rate constants. For Pd catalysed runs, it was found that olefinic hydrochlorination rate is more dependent on H_2 pressure than the aromatic chlorine reaction rate, and that the aromatic rate was favored at low pressures. Selectivities were insensitive to temperature in the range 20 to 100°C for both Ni and Pd catalysed reactions.

(iii)Catalyst Loading and Stirrer Speed

Variation of the stirrer speed did not significantly affect initial rates or intermediate selectivities, indicating that mass transfer limitation did not occur over the range of speeds studied.

For the Pd catalyst, it was found that initial DDE reaction rate is not proportional to catalyst loading as would be expected at low levels of catalyst. It was proposed (12) that this was due to poison of some of the catalyst by impurities. Due to this effect, all other Pd and all Ni catalysed experiments were conducted at higher levels of catalyst loading.

iv) Effect of Hydrogen Pressure and Temperature

DDE reaction rates in both Ni and Pd catalysed experiments were not accurately described by simple power law kinetics. Attempts were made to describe the effect of changes in hydrogen pressure on the rate of DDE disappearance for Pd catalysed reactions. A log-log plot of initial rate

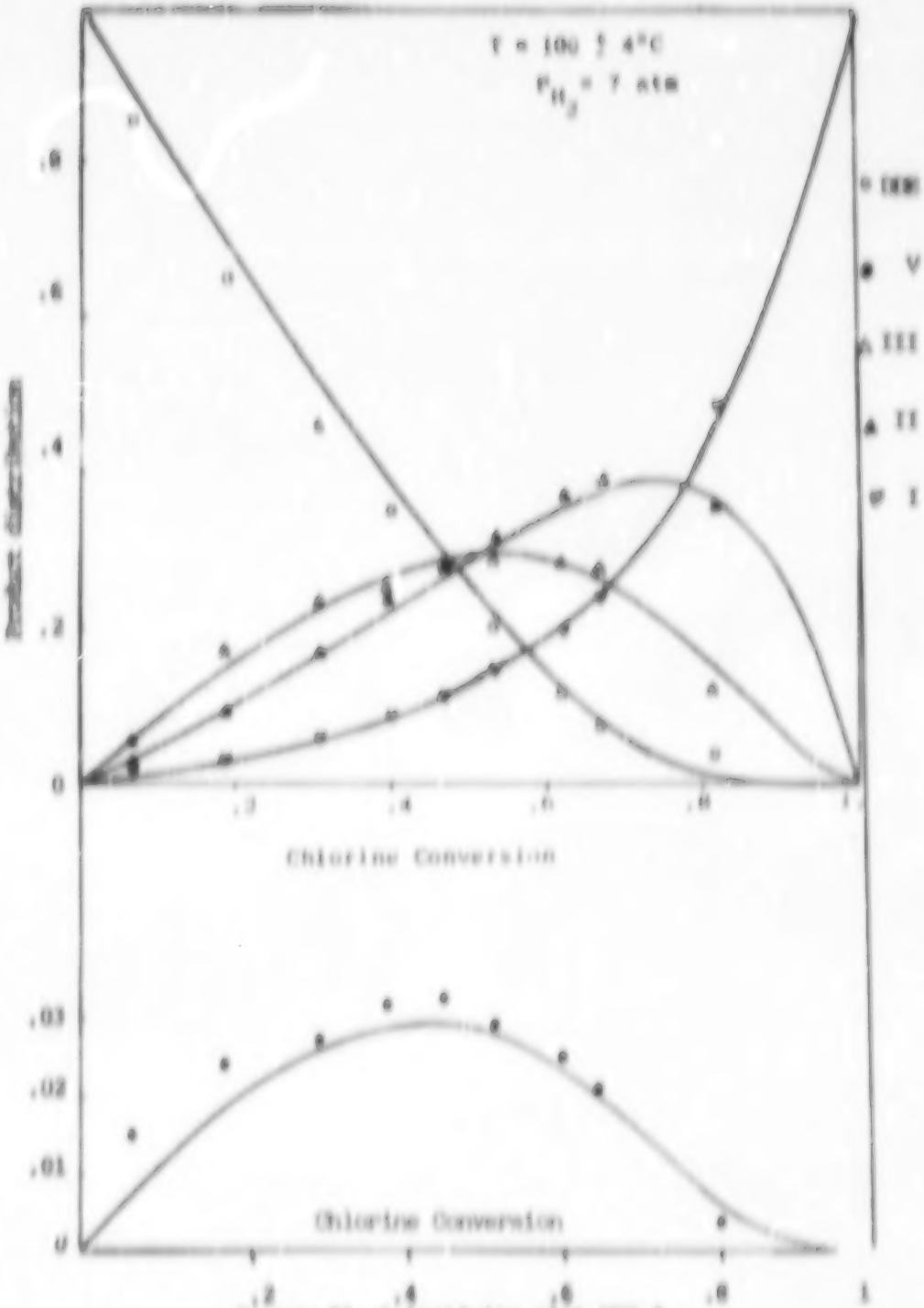


Figure 20. Selectivity plot [illegible]

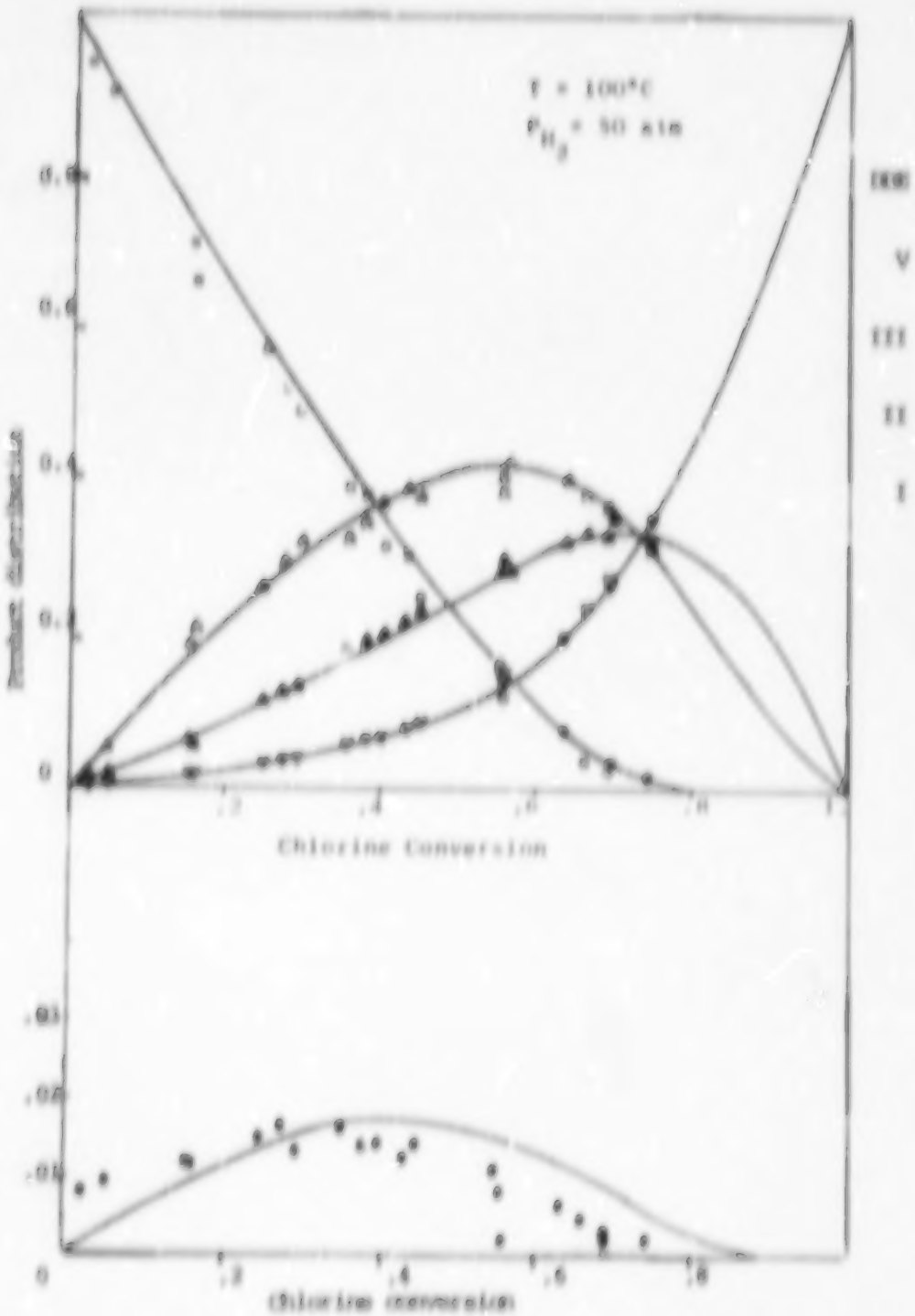


Figure 21. Selectivity plot for 2, 4.

versus H_2 pressure had a slope of 0.72.

The kinetic behavior of Ni-catalyzed IBB hydrodechlorination is quite different. The IBB concentration versus time curves are characterized by: 1) an induction period; 2) zero order behavior at intermediate conversions; and 3) a shift to higher order reactionality at high conversions. The nickel catalyst requires reduction (33) and it was found that the length of the induction period could be shortened by increasing pretreatment temperature. The induction period may also be due to product desorption rate limitation (34). The remaining characteristics are consistent with the adsorption reaction model of a disappearing component.

C. ALDRIN AND DIELDRIN

Pulsed microreactor and high pressure liquid phase reactions were carried out to determine hydrodechlorination activity of aldrin and dieldrin.

Gas Phase Pulsed Microreactor

A set of six aldrin hydrodechlorination experiments were conducted at a single temperature (220°C), pressure (2.1 atm), and space time (.01 seconds). The first two experiments investigated thermal reactions in the empty reactor with He and H_2 carrier gas. The remaining four experiments were conducted with H_2 carrier gas, Al_2O_3 support and varying concentrations (0.00, 0.05, 0.10, 0.35 wt%) of Ni catalyst. No thermal reaction occurred but Al_2O_3 with no Ni converted 11% of aldrin to a less volatile compound (aldrin with one olefin hydrogenated). As the concentration of Ni increased, hydrogenation was quantitative while hydrodechlorination proceeded in parallel. Aldrin chlorine was not highly reactive. One experiment using hexachlorocyclopentadiene showed nearly complete hydrodechlorination indicating that steric effects are important in aldrin dechlorination.

Liquid Phase Experiments

A set of preliminary dieldrin hydrodechlorination experiments were conducted in the rocking autoclave. All employed Ni catalyst while temperature, H_2 pressure, time, and catalyst concentration were varied. The major conclusion was that only at high temperature, high H_2 pressure and high catalyst concentration were significant amounts of completely hydrodechlorinated product formed. Initial hydrogenation of the olefin was not observed which was consistent with the IBB results.

Two experiments were conducted in the teflon-lined autoclave to determine the reactivity of aldrin and dieldrin. The conditions were the same for both experiments. Detailed analysis was not completed, but results indicate that the aldrin olefin is hydrogenated and two chlorines removed, before the reaction slows down. Dieldrin is not hydrogenated but does lose two chlorines before the reaction stops. More severe conditions are required for further reaction.

D. TOXAPHENE

Toxaphene is a mixture of polychlorinated camphenes. Most of the chlorine is aliphatic in nature. Thousands of isomers exist (34-36), precluding quantitative analysis based on number of chlorine atoms per molecule.

Liquid Phase Experiments

Four experiments were performed to determine overall reactivity. All were performed at the same temperature, H_2 pressure, and ratio of weight of catalyst to weight of toxaphene. Reaction time varied. Under these conditions, most chlorine was removed in the first two hours and molecules containing only one or two chlorine atoms were resistant to further hydrodechlorination. Toxaphene was more easily hydrodechlorinated than aldrin or dieldrin, even though most of the chlorine is aliphatic. This further substantiates the belief that steric factors account for the non-reactivity of aldrin and dieldrin.

SECTION 6

PROCESS DESIGN

Final design of a hydrodechlorination process is beyond the scope of this project but quantitative features of the process may be proposed with the aid of the data outlined.

Qualitative Aspects

Due to the variability of the pesticide and solvent compounds to be processed, a batch process is indicated in spite of the possible advantages of continuous systems. This same variability in the volatility of the feed favors liquid phase processing. Ethyl alcohol is recommended as a solvent over p-xylene because it is a better solvent for the acid acceptor, and having lower vapor pressure, it will contribute less to the pressure in the liquid phase reactor. Although catalyst life under service conditions has not been determined, the Girdler G49A nickel on kieselguhr used in this study was satisfactory for both economic and activity reasons. Operation with the HCl as a by-product is unacceptable, and NaOH as acid acceptor was found to be superior to $Ca(OH)_2$. Details of product recovery will depend on the nature of the feed and the severity of the processing.

Quantitative Aspects

Operation at high temperature is favored on the basis of rate considerations, but processing complications indicate that operation at around 100°C is preferred. The solution step should be carried out at atmospheric pressure, while the attainment of reasonable rates in the reactor will require a partial pressure of H_2 of 20 to 50 atmospheres.

Process Description

A conceptualized batch process employing ethanol, sodium hydroxide, catalyst and hydrogen is given in Figure 22. The process includes extractive solution of pesticides in ethanol, reaction at high H_2 pressure, recovery of ethanol and extractive removal of soluble inorganics from the waste stream.

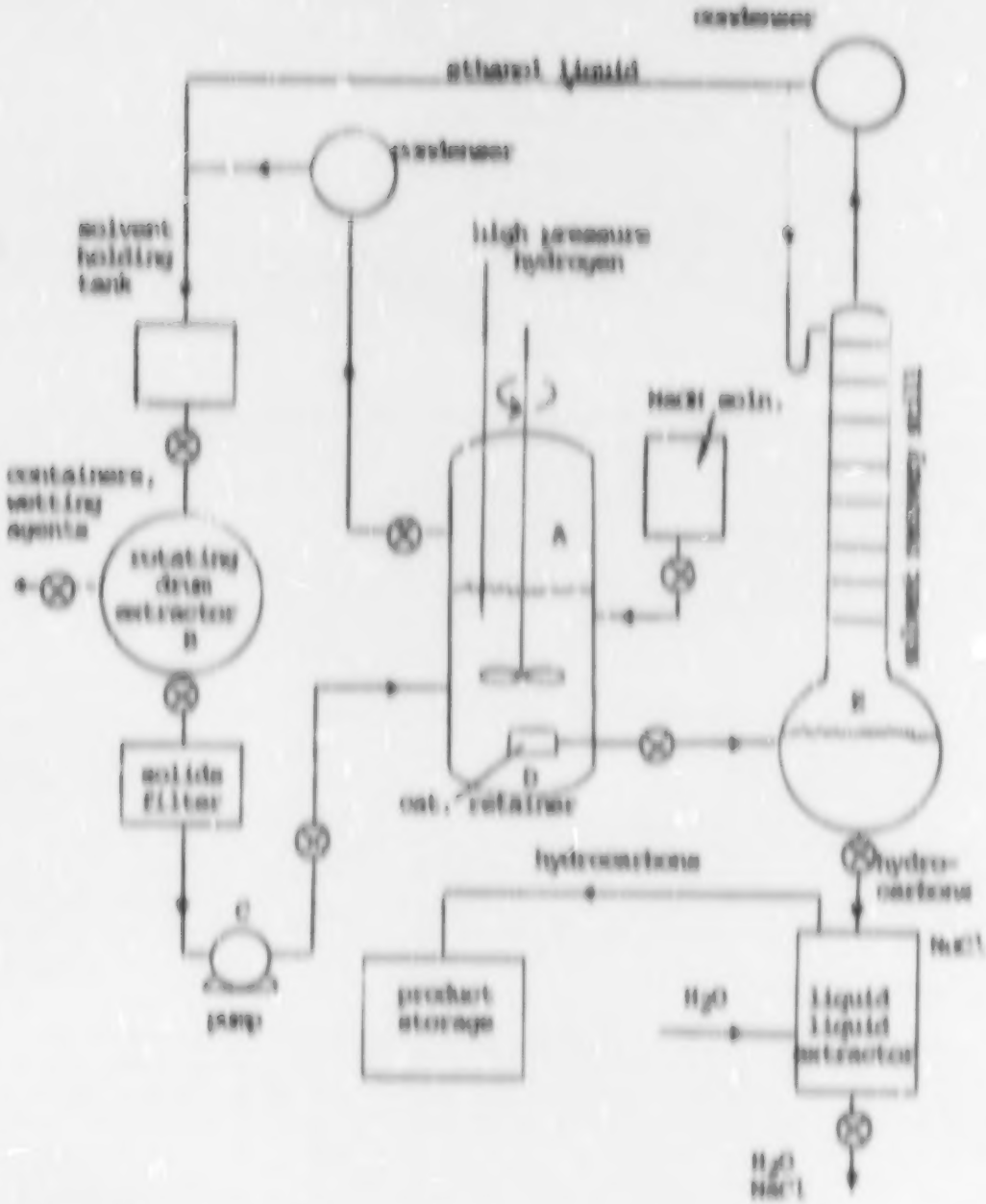


Figure 22. Pesticide detoxification process flow sheet.

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